THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 6th, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read for the first time in favour of:—Reginald Haydn Hopkins, D.Sc., F.I.C., and William Basil Walker, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Edward Bertram Anderson, M.Sc., F.I.C., Edward Foster Eaton, Frank Maudsley, B.Sc., F.I.C., James William Thom, B.Sc., and Samuel Gordon Stevenson, B.Sc., B.Pharm., F.I.C.

The following were elected Members of the Society:—Alan Arthur Douglas Comrie, B.Sc., A.I.C., Edwin William Stanley Press, B.Sc., A.I.C., and Muriel Roberts, B.Sc., F.I.C.

The following papers were read and discussed:—"The Estimation of Hormones," by K. Culhane, B.Sc., A.I.C., and S. W. F. Underhill, M.A., B.M., B.Ch.; "The Chemical Assay of Thyroid Gland," by G. Middleton, B.Sc., A.I.C.; "The Water-Protein Ratio of Lean Meat, and its Bearing upon the Analysis of Sausages," by F. W. Jackson, B.Sc., A.I.C., and Osman Jones, F.I.C.; "Nitrite in Cured Meats," by Osman Jones, F.I.C.; and "Notes on the Freezing Point of Milk," by H. C. Lockwood, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION

A JOINT Meeting of the Section with the Liverpool and Manchester Sections of the Institute of Chemistry and other bodies was held in Manchester, on April 9th, 1932.

In the absence of the Chairman (Mr. J. Evans), Prof. W. H. Roberts presided over a large attendance. Dr. G. Roche Lynch gave a lecture on "Poisons and Poisoning," which was followed by a discussion.

Obituary

SIR WILLIAM SMITH

WE regret to record the death, on March 17th, of Sir William Robert Smith, who had been a Member of the Society since 1892.

Sir William was born in 1850, and, after graduating in medicine at Aberdeen, became Medical Officer to the old London School Board. In 1886 he founded the British (now the Royal) Institute of Public Health, and for the rest of his life his work was closely associated with that of the Institute, of which, at the time of his death, he was still Principal. In addition to his work in connection with that Institute, he held the appointments of Public Analyst for the County of Berkshire, the Boroughs of Newbury and New Windsor, the Metropolitan Boroughs of Paddington and Woolwich, and the City of Oxford.

He was also Emeritus Professor of Forensic Medicine and Toxicology at King's College, London, and he edited the seventh edition of Guy and Ferrier's *Forensic Medicine*.

In 1918 he was knighted, after serving as Sheriff of the City of London.

The Council has sent, on behalf of the Society, a letter of sympathy to Lady Smith.

EDITOR.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXII. The Separation of the Earth Acids from Metals of the Hydrogen Sulphide Group

BY E. F. WATERHOUSE AND W. R. SCHOELLER, PH.D.

(Work done under the Analytical Investigation Scheme)

(Read at the Meeting, November **4, 1931**)

THE mineral associates of the earth acids in the hydrogen sulphide group are: (1) antimony (in stibiotantalite); (2) bismuth (in bismuthotantalite); (3) tin (subordinate amounts in most earth-acid minerals); (4) lead (less than one per cent.) accompanies uranium; and (5) copper (very small amounts in a few minerals). Arsenic, selenium, tellurium, silver, mercury, and cadmium cannot be described as mineral associates of the earth acids. Germanium may be present in traces, but its isolation calls for a special procedure and for substantial quantities of material.

In endeavouring to work out a separation process of practical value, we decided that, as the process would be preceded by the decomposition of the mineral, the test analyses should be made by the same procedure; since, by mixing

separately-prepared solutions of known metal content, we should be disregarding the possibility of complex-formation during the lixiviation of the melt. Hence also, the completeness of the separation should be proved by the quantitative recovery of the earth acids as well as of the metals of the hydrogen sulphide group.

Now the decomposition procedure proposed by Schoeller and Powell (I, ANALYST, 1922, **47**, 93), and applied in the present investigation, is fusion with bisulphate, followed by lixiviation with tartaric acid. In this process, any lead present is converted into and eliminated as insoluble sulphate, together with silica and the bulk of the stannic oxide. The filtrate is saturated with hydrogen sulphide, and the precipitate examined for any member or members of the group. Of these, lead has already been removed as sulphate. The separation of tin from the earth acids has been discussed in Section XX (ANALYST, 1931, **56**, 795). There remain antimony, bismuth, and copper to be considered in this Section. In a process effecting a satisfactory separation of these metals as sulphides from the earth acids, it may, we submit, be taken for granted that any small quantities of tin (arsenic) present in the solution will accompany the antimony, and any traces of lead, silver, etc., the bismuth and copper.

A. ANTIMONY AND EARTH ACIDS.—Two time-honoured but ineffective procedures (Berzelius; Rose) for the separation of tin and antimony from the earth acids have been criticised in an earlier Section (VIII, ANALYST, 1927, **52**, 507, 509); hence further discussion of them is unnecessary.

Foote and Langley's Process.—A separation process which, no doubt, combines accuracy with simplicity, is given by Foote and Langley for the analysis of stibiotantalite (*Amer. J. Sci.*, 1910, **30**, 398). It consists in dissolving the powder (1 grm.) in 20 c.c. of hydrofluoric acid, diluting to 300 c.c., and passing a stream of hydrogen sulphide. The precipitate is treated with ammonium sulphide for the separation of a little bismuth from the antimony sulphide. The fluoride filtrate is evaporated with sulphuric acid, diluted, and the earth acids precipitated with ammonia.

We do not wish to criticise Foote and Langley's method, but submit that the process given below is more generally applicable, and does not involve the use of hydrofluoric acid.

Authors' Investigation.—Our first test analyses by Schoeller and Powell's method (*vide supra*) disclosed a variable, but appreciable, shortage in the earth-acid recovery. The mixed oxides were fused with bisulphate, the clear tartaric solution of the melt treated with hydrogen sulphide, and the antimony in the sulphide precipitate determined volumetrically by permanganate. The filtrate from the antimony sulphide was submitted to tartaric hydrolysis, followed by tannin precipitation (XIX, ANALYST, 1931, **56**, 306). By re-treating the sulphide precipitate we proved that it contained earth acid; in a few experiments the amount of earth acid occluded in the sulphide precipitate was determined separately, with the following results: 0·0057; 0·0036; 0·0046; and 0·0022 grm. In our experience, metallic sulphides precipitated from acid tartrate solution containing earth acid are invariably thus contaminated.

This may be explained by the following considerations: Tartaro-tantalic

acid (and, in a lesser degree, tartaro-niobic acid) is a rather unstable complex, subject to hydrolytic dissociation in acid solution; thus, when a large excess of mineral acid is added to the boiling solution, the earth acid is almost quantitatively precipitated ("tartaric hydrolysis"). In cold, weakly acid solution, partial dissociation takes place gradually with formation of a colloidal phase, and the solution, even though quite clear at first, eventually deposits a flocculent precipitate. The flocculation of the earth acid is, no doubt, assisted by that of the sulphide precipitate, and accelerated by warming and by the coagulating effect of hydrogen sulphide. In the same way, contamination of hydrogen-sulphide precipitates with titania can be brought about in weakly acid sulphate solutions.

In the next series of tests we proceeded as follows: Solution of the sulphide precipitate in strong sulphuric acid; permanganate titration; re-precipitation of antimony sulphide, filtration; volatilisation of the antimony by heating the precipitate with bromine and hydrochloric acid; recovery of the co-precipitated earth acid from the residue combined with the sulphide filtrate. This rather elaborate procedure was abandoned as being applicable to antimony (tin), but not to the hydrogen sulphide group as a whole.

A quantitative separation was finally achieved by a re-treatment in ammoniacal solution, included in the following sequence of manipulations: Solution of the sulphide precipitate in sulphuric acid; addition of tartaric acid and excess of ammonia; treatment with ammonium polysulphide; acidification with acetic acid, boiling, and filtration. The re-precipitated sulphide was now free from earth acids, which were found in the filtrate.

The treatment just outlined not only separates antimony from the earth acids, but also forms the basis of the group separation procedure described below.

B. Bismuth and Earth Acids.—So far as we know, the only reference to bismuth in the literature on the subject occurs in Meyer and Hauser's monograph, *Die Analyse der seltenen Erden und der Erdsäuren* (p. 271); the passage merely states that pyrosulphate hydrolysis (*cf.* XII, Analyst, 1928, **53**, 467) affords a good separation of the earth acids and titania from most metallic elements, with the exception of tin, tungsten, silicon, bismuth, mercury, lead, and the alkaline earths.

The recent discovery of bismuthotantalite (*Min. Mag.*, 1929, **22**, 185), a mineral rich in bismuth and analogous to stibiotantalite, rendered a study of the separation of bismuth from the earth acids desirable. We proceeded as for the separation of antimony from the earth acids, the first bismuth sulphide precipitate (which always contained a little earth acid) being dissolved in sulphuric acid, the liquid treated with tartaric acid and excess of ammonia, and poured into ammonium sulphide. The re-precipitated sulphide was collected, dissolved in hot dilute nitric acid, and the bismuth determined by our modification of the phosphate method (Analyst, 1920, **45**, 435). When igniting the sulphur globules, resulting from the nitric acid attack on the second bismuth sulphide, we invariably obtained a mgrm. (more or less) of residue which was identified as earth acid, and added to the main fraction. Hence, the process gives a more perfect separation with antimony than it does with metals the sulphides of which are insoluble in ammonium sulphide, such as bismuth and copper (*vide infra*).

C. COPPER AND EARTH ACIDS.—For the sake of uniformity in procedure, our tests with copper oxide were conducted in precisely the same manner as those with antimony and bismuth. The copper was, therefore, necessarily recovered in two fractions, the one soluble, the other insoluble, in ammonium polysulphide. The former was re-precipitated, like antimony sulphide, by boiling with acetic acid. The combined precipitates were dissolved in nitric acid, the solution evaporated, diluted, filtered, and electrolysed for copper, while the small sulphur residue was ignited, leaving, in each case, about 1 mgrm. of pentoxides.

D. THE SEPARATION.—For the separation of the hydrogen sulphide group metals from the earth acids we advocate the following process: The mineral (0·25 to 0·5 grm.), or the mixture of the oxides (about 0·2 grm. M_2O_5) is fused with 3 to 4 grms. of potassium bisulphate in a 50 c.c. silica crucible, and the resulting mass dissolved in tartaric acid or ammonium tartrate, as described in XIX (*loc. cit.*).

In the case of minerals, the acid solution is allowed to stand for an hour, then freed by filtration from the deposited stannic oxide, lead sulphate, silica and, possibly, unattacked mineral. If necessary, the fusion and lixiviation are repeated on the ignited residue, after previous extraction with ammonium acetate to remove lead sulphate, if present.

The clear liquid is treated at 60° C. with hydrogen sulphide, and left in a warm place for an hour to clear. The sulphide precipitate, SP^1, is collected, and washed with 2 per cent. sulphuric acid containing hydrogen sulphide; the filtrate is concentrated by evaporation.

Treatment of SP^1.—Filter and precipitate are returned to the beaker, and warmed with 8 c.c. of strong sulphuric acid, with repeated dropwise addition of nitric acid, till the organic matter is destroyed. The oxidant is completely expelled by strong heating. The mass, when cold, is treated with 10 c.c. of 20 per cent. tartaric acid solution and 25 c.c. of warm water. Ammonia in moderate excess is added, and the liquid poured slowly into fresh yellow ammonium sulphide; hydrogen sulphide is passed for a few minutes, and the beaker allowed to stand on a covered water-bath for an hour or more.

Treatment of SP^2.—If sulphides insoluble in ammonium sulphide (SP^2) have separated, they are collected, washed with dilute ammonium sulphide, and dissolved in hot dilute nitric acid, which is evaporated. The residue is taken up with dilute acid, and the solution filtered through a small paper, which is washed with dilute acid and transferred to a tared porcelain crucible *C*. The filtrate is analysed for bismuth and copper (traces of lead) by the usual methods.

SP^3.—The clear yellow ammonium sulphide solution (or filtrate from SP^2) is acidified with acetic acid, boiled, treated with hydrogen sulphide, and left to clear. The precipitate, SP^3, is collected and washed as before, and the filtrate concentrated by evaporation. SP^3 is returned to the beaker with the paper, heated with 10 c.c. of strong sulphuric acid and several grms. of potassium sulphate till the acid mass is perfectly colourless. After dilution and suitable acidification with hydrochloric acid the antimony is titrated with permanganate. The titrated

liquor is treated with iron wire, and the precipitate examined for copper; the filtrate is tested with hydrogen sulphide for tin.

Earth-Acid Recovery.—The bulk of the earth acids is precipitated by tartaric hydrolysis as *HP* in the concentrated filtrate from *SP*[1]; the filtrate from *HP* is added to that from *SP*[3], and the balance of the earth acids precipitated therefrom as *TP* (XIX, *loc. cit.*, C, E, F). The precipitate *TP* is strongly ignited in crucible *C*, containing the small residue from *SP*[2], then warmed with 1:1 hydrochloric acid till white (it is usually pink, being contaminated with a trace of iron), and collected on a 7 cm. filter. The precipitate, *HP*, is then ignited in the same crucible, leached with acidified water, and added to *TP*. The combined precipitates are strongly ignited in crucible *C*, and weighed; the ash of several filters has to be subtracted from the weight.

RESULTS OF TEST SEPARATIONS.—In every test analysis given below, the quantitative composition of the oxide mixture (in no case were the oxides fused and leached separately) was unknown to the operator. The two M_2O_5 fractions, *HP* and *TP*, are given separately, as we wish to record and briefly discuss the *HP*:*TP* ratio. The weight of *TP* includes any small recoveries of pentoxide from *SP*[2]. (The figures represent grms.)

	Taken.		Found.	*HP*.	*TP*.	Found.	M_2O_5.	Sb_2O_3.
Exp.	M_2O_5.	Sb_2O_3.	Sb_2O_3.	Net.	Net.	M_2O_5.	Error.	Error.
Ta 1	0·2638	0·0238	0·0238	0·2356	0·0282	0·2638	0·0000	0·0000
,, 2	0·2022	0·0618	0·0616	0·1728	0·0291	0·2019	−0·0003	−0·0002
,, 3	0·1515	0·1266	0·1251	0·1263	0·0255	0·1518	+0·0003	−0·0015*
Nb 4	0·2169	0·0607	0·0614	0·1888	0·0276	0·2164	−0·0005	+0·0007
,, 5	0·1720	0·1152	0·1144	0·1471	0·0244	0·1715	−0·0005	−0·0008
		Bi_2O_3	Bi_2O_3					Bi_2O_3
Ta 6	0·1780	0·1024	0·1025	0·1365	0·0406	0·1771	−0·0009	+0·0001
,, 7	0·1370	0·1284	0·1271	0·0600	0·0770	0·1370	0·0000	−0·0013
,, 8	0·2002	0·0721	0·0722	0·1608	0·0389	0·1997	−0·0005	+0·0001
Nb 9	0·2089	0·1826	0·1834	0·1639	0·0455	0·2094	+0·0005	+0·0008
,, 10	0·1006	0·1497	0·1486	0·0720	0·0286	0·1006	0·0000	−0·0011
		CuO	CuO					CuO
Ta 11	0·1400	0·0592	0·0590	0·1285	0·0111	0·1396	−0·0004	−0·0002
Nb 12	0·2039	0·0675	0·0670	0·1728	0·0308	0·2036	−0·0003	−0·0005
EA 13 { Taken:	M_2O_5	0·1504;	Sb_2O_3	0·0785;	Bi_2O_3	0·1012.		
Found:	,,	0·1505;	,,	0·0780;	,,	0·1012.		

* *Exp.* 3: Sb_2S_3 filtered off too soon; proved minute amount of Sb in ignited *HP* by applying our method.

Ratio of HP to TP.—It will be observed that the proportion of earth acid recovered in these tests as *HP* by tartaric hydrolysis is much lower than that obtained in the earlier investigation of tartaric hydrolysis, where it was found that "precipitation is complete but for a few mgrms." (XVI, ANALYST, 1929, **54**, 708). The explanation is, that the solutions submitted to tartaric hydrolysis in the present investigation contained more tartaric and sulphuric acids—necessarily introduced in the process of solution—than those tested in Section XVI, either acid causing less complete precipitation. The observation has a certain practical importance, and will be borne in mind when we apply our methods to the analysis of minerals.

The original procedure proposed by Schoeller and Powell for the separation of the earth acids from the hydrogen sulphide group is described in Hillebrand and Lundell's *Applied Inorganic Analysis* (ANALYST, **1930**, **55**, **351**), wherein it is stated that the method gave "perfect separations of antimony, tin, lead and copper, from solutions containing as much as 0·1 grm. each of Sb_2O_5 and Ta_2O_5" (p. 470, footnote 17). This statement is at variance with the observations recorded in this Section. That the metals of the hydrogen sulphide group are quantitatively precipitated is not questioned, but we repeat that the precipitate, in our experience, always carries a little earth acid; and we are of opinion that it should always be re-treated by the method described above.

SUMMARY.—The separation of tantalum and niobium from antimony, bismuth, and copper was studied. When the mixed oxides were fused with bisulphate, the mass dissolved in tartaric acid, and the clear solution treated with hydrogen sulphide, the sulphide precipitate was always found to be contaminated with a few mgrms. of earth acid. The co-precipitation is ascribed to hydrolytic decomposition of the tartaric earth-acid complexes. The separation is completed by further treatment of the sulphide precipitate; this is dissolved in strong sulphuric acid, tartaric acid and excess of ammonia are added, and the solution is poured into ammonium sulphide. Bismuth and copper sulphides are precipitated; the filtrate is acidified with acetic acid, giving a precipitate of antimony sulphide. The small fraction of earth acid occluded in the original sulphide precipitate is found in the filtrate from the antimony precipitate. Directions are given for the quantitative recovery of the earth acids.

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DISCUSSION

Dr. B. S. EVANS said that he had often had occasion to separate the hydrogen sulphide group from tantalum and niobium, and had so far to assume that the separation was fairly complete; now, of course, he must revise that. He was quite aware that tartaric acid complexes were unstable in acid solution; in fact, if one added excess of acid and boiled, one noticed that earth acids would come down, whereas the same did not occur with oxalic acid. He noticed that oxalo-complexes were precipitated by alkali, but not by acids. He wondered, therefore, if the separation were carried out in oxalic, instead of tartaric, solution, if the same occlusion of earth acid would take place. The only difficulty, presumably, would be tin, the sulphide of which was held in solution by oxalic acid; he was on the point of publishing a paper showing that stannous sulphide could be precipitated satisfactorily in alkaline oxalate solution. He strongly deprecated the use of ammonium sulphide for the separation of antimony from, for example, lead; antimony sulphide was certainly soluble in very strong ammonium sulphide, but the solution was uncertain and precarious. It did not seem to be widely known that one could precipitate antimony sulphide from its solution in sodium sulphide by the mere addition of ammonium chloride. He had good reasons for disliking ammonium sulphide separations altogether.

Dr. J. GRANT asked if Dr. Schoeller had had occasion to determine the optimum *p*H values at which hydroxides and sulphides precipitated. Most common metals had a definite *p*H range at which they were brought down, but

there were no data available regarding niobium and tantalum, and he thought this would be very useful.

Dr. SCHOELLER, in reply, invited Dr. Evans to test sulphide precipitates, obtained from tartrate solutions containing earth acids, by the method described in the present paper. He was not prepared to say that such sulphide precipitates would invariably prove to occlude earth acid; but he thought it safest, in all accurate work, to re-treat the sulphides as described. He was fully aware that oxalo-complexes were more stable in acid solution than tartaro-complexes, but had refrained from using the former because oxalic acid prevented the precipitation of tin by hydrogen sulphide.

In reply to Dr. Grant's inquiry, he thought that the question of the pH values of solutions containing organic complexes of the earth acids was so involved that he and his collaborators had come to the conclusion that such measurements would not help them in their task. The determination of pH values was, no doubt, most useful in a study of the precipitation of sulphides and hydroxides of common metals from simple mineral acid solutions; but he and his collaborators were dealing with solutions containing much organic acid and soluble complexes of various amphoteric oxides, as well as salts and mineral acid. His personal feeling was that the pH value of such solutions, even if accurately known, was only one of several factors affecting the operations.

Methods for the Chemical Examination of Dyed Leathers for the Presence of Diamines and Aminophenols

BY F. E. HUMPHREYS, PH.D., A.R.C.S., A.I.C., AND
H. PHILLIPS, D.SC., F.I.C.

IN several cases of dermatitis, alleged to have been caused by dyed leather used for clothing and hat-bands, it has been found necessary to examine the leathers for the presence of para- and meta- diamines and aminophenols. These organic bases are not commonly used, as such, for the purpose of dyeing leather. They are, however, used in the manufacture of certain leather dyestuffs, and among leather dyers and users it has been assumed that traces of these compounds may pass unchanged through the dye-manufacturing process, and be present in the finished dyestuff.

Valuable tests for the detection of diamines and aminophenols in extracts of fur have been published by Cox (ANALYST, 1929, **54**, 694) and by Forster and Soyka (*J. Soc. Dyers and Colourists*, 1931, **67**, 99; ANALYST, 1931, **56**, 476). These and other tests have been applied to the detection of para- and meta- phenylene-diamines in leather extracts by Callan and Strafford (ANALYST, 1931, **56**, 625), who found that some of them gave misleading information, owing to the presence of tannins in the extracts, and concluded that only a limited number of the tests were applicable. Even in these cases the result should be confirmed by applying the test to the leather extract after the addition of very small amounts of the suspected diamine.

The methods employed for dyeing and colouring clothing and hat-band leathers vary from factory to factory, and a large number of complex substances and mixtures are frequently applied to the leathers in order to fix the dyestuff and to obtain a special "finish." Extracts of such leathers may contain not only tannins, but also other complex substances derived from the fixing and finishing materials. For these reasons it will always be difficult to draw definite conclusions from tests made directly on leather extracts.

Methods have, therefore, been investigated, by which diamines and aminophenols may be recovered from leather and leather extracts, and thus obtained free from tannins and other substances liable to interfere with the tests. For this investigation specially treated leathers have been used. Known volumes of standard solutions of the hydrochlorides of diamines and aminophenols were applied to vegetable-tanned sheepskin leathers and dyed and undyed semichrome leathers (*i.e.* leathers which have been vegetable-tanned, stripped and re-tanned with chromium compounds), and the leathers allowed to dry in air. In this manner, samples of dyed and undyed leathers containing known amounts of the organic bases were obtained.

The tests used in the present investigation were those described by Cox (*loc. cit.*), and the additional tests suggested by Callan and Strafford (*loc. cit.*). The reagents employed were made up as described by Callan and Strafford; the volumes of these reagents used, irrespective of the concentration of the solution under examination, were as follows:

No. 1. *Nitrous Acid.*—To the solution 0·5 ml. of 2 *N* hydrochloric acid is added, followed by 0·5 ml. of 0·5 *N* sodium nitrite solution.

No. 2. To the mixture obtained in Test 1, 5·0 ml. of 0·05 *N* alkaline solution of β-naphthol are added.

No. 3. *Sodium Hypochlorite.*—To the solution, made faintly alkaline with 0·1 *N* sodium hydroxide solution, 1 ml. of dilute sodium hypochlorite solution is added.

No. 4. *Phenol and Hypochlorite.*—To the solution, made faintly alkaline with 0·1 *N* sodium hydroxide solution, 1 ml. of 5 per cent. phenol solution is added, followed by 2 to 5 drops of dilute sodium hypochlorite solution.

No. 5. *p-Dimethylaminobenzaldehyde.*—To the solution, acidified with 0·2 ml. of 2 *N* hydrochloric acid, 1 ml. of a 1 per cent. alcoholic solution of the reagent is added.

No. 6. *Ferric Chloride.*—To the neutral solution 1 drop of a 10 per cent. solution of ferric chloride is added.

No. 7. *Diazobenzene-p-sulphonic Acid.*—To the solution 1 grm. of sodium acetate crystals is added, followed by 1 ml. of 0·05 *N* diazobenzene-*p*-sulphonic acid solution.

No. 8. *Aniline and Dichromate.*—To the solution, acidified with 1 ml. of 2 *N* hydrochloric acid, 1 ml. of a 1 per cent. aniline hydrochloride solution is added, followed by 1 drop of 5 per cent. potassium dichromate solution.

The tests were carried out in Nessler cylinders, and the colorations obtained were compared with those given by solutions of diamines and aminophenols of

known concentration. By this means the amount of the diamine or aminophenol which had been recovered from the sample of leather was determined approximately.

Attempts to determine the amount of harmful organic base present in extracts of leathers, alleged to have caused dermatitis, frequently revealed that it was impossible to match exactly the colorations obtained with very dilute solutions of diamines and aminophenols. Had these determinations not been attempted, the colorations might have been regarded as positive results. Further, it was found that some of these colorations could be accurately matched by using very dilute solutions of harmless bases.

The causes underlying the action of *p*-phenylenediamine and similar compounds on skin have been the subject of considerable discussion (Parsons, *Reports on Public Health and Medical Subjects*, 1924, No. 27; Cox, *loc. cit.*; Percival, *Lancet*, 1931, **221**, 417). Although the action of *p*-phenylenediamine has frequently been ascribed to semi-oxidised forms of the base, no reference has hitherto been made to the wide use of dimethyl-*p*-phenylenediamine and *p*-phenylenediamine for the study of the oxidation processes in animal and vegetable tissues. When placed in contact with such materials, dimethyl-*p*-phenylenediamine is oxidised to a reactive quinone-imine which condenses with naphthol, forming an indophenol blue, whilst *p*-phenylenediamine is probably converted into a quinone di-imine, which forms a purple compound, analogous to quinhydrone, by condensation with an unchanged molecule of diamine. Szent-Györgyi (*Biochem. Z.*, 1925, **157**, 79) found that this purple addition compound was reduced to a colourless compound (probably the diamine) by lactic acid, with the addition of washed muscle, and suggested that *p*-phenylenediamine could act as a carrier between the oxygen activators and dehydrogenases in the cell. These and other experimental results (Harrison, *Biochem. J.*, 1929, **23**, 982) suggest that the diffusion of *p*-phenylenediamine or its quinone di-imine into the cells of the skin might seriously affect their oxidation-reduction processes. Possibly such compounds can interfere with the functions of the cell-catalysts, and in this way divert or arrest some chain of vital reactions.

On the basis of this interpretation, it would appear that *p*-phenylenediamine and its partly oxidised products are equally obnoxious, and that the susceptibility of different people to the diamine may increase as the resistance of their skins to penetration by the diamine or its oxidation products decreases.

The Recovery of Diamines and Aminophenols from Specially Treated Vegetable-tanned and Semichrome Clothing Leathers

(*a*) *By Distillation in a Current of Super-heated Steam.*—Tannins and complex dyestuffs are not volatile in a current of super-heated steam, whereas a large number of dyestuff intermediates can be separated under these conditions. The distillate from a piece of leather containing dyestuff volatile intermediates, therefore, consists of a colourless, dilute solution of those intermediates.

The leather samples, prepared as described, were cut into small pieces, and these were placed in a flask, together with distilled water (75 ml.) and saturated sodium carbonate solution (2 ml.). A current of super-heated steam (200° C.) was

passed into the boiling mixture until 250 ml. of distillate had been obtained. This was filtered, and aliquot portions (25 to 40 ml.) were then examined in Nessler cylinders by means of the tests enumerated on p. 291.

One serious objection can be raised to this method (see Cox, ANALYST, **1931, 56**, 633). It is possible that, under the combined influence of super-heated steam and decomposing leather, normally stable complex dyes might be reduced or resolved into intermediates. If this possibility is borne in mind, distillation in super-heated steam forms a useful preliminary method of examination.

In Table I the results obtained with the prepared leather samples are given. In the last column of this Table, the tests which were positive are recorded, the figures in brackets indicating the amount (in mgrms.) of the diamine or aminophenol found, and those printed in italics the test or tests by which the amounts were determined.

TABLE I

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM LEATHERS BY MEANS OF SUPER-HEATED STEAM

Diamine or aminophenol.	Weight of diamine or aminophenol added to leather. Mgrms.	Nature of leather.	Weight of leather. Grms.	Positive tests given by:
p-Phenylenediamine	10·0	Vegetable-tanned sheepskin	20·0	4, 5, 8
,,	7·0	,, ,,	5·0	Nil
,,	7·5	,, ,,	7·5	4, *5*, 8 (0·15)
,,	5·0	,, ,,	8·3	4, 8
m-Phenylenediamine	5·0	Vegetable-tanned sheepskin	7·0	*1*, 7 (0·15)
,,	5·0	Dyed semichrome	6·5	*1*, 7 (0·10)
m-Toluylenediamine	5·0	Vegetable-tanned sheepskin	6·1	*1*, 4, 7 (0·60)
,,	5·0	Undyed semichrome	7·0	*1*, 7 (0·18)
,,	5·0	Dyed semichrome	5·7	*1*, 7 (0·06)
Metol	5·0	Vegetable-tanned sheepskin	4·2	4
,,	5·0	Dyed semichrome	6·3	*4* (0·06)
p-Aminophenol	5·0	Vegetable-tanned sheepskin	11·5	4, 6
,,	5·0	Dyed semichrome	6·0	4

Reliance cannot be placed on Test 4, because the steam distillate from a sample of leather, to which no diamines had been added, gave a blue coloration when this test was applied. The distillates from the leathers which had been treated with the *o*- and *m*-aminophenols and amidol failed to give distinctive reactions.

(*b*) *By the Continuous Extraction of Extracts of the Leather with Benzene.*— The samples of leather were extracted by two methods: by placing the leather (cut into small pieces) in 40 ml. of 1 per cent. acetic acid for 18 hours, or in 40 ml. of 0·1 *N* hydrochloric acid for 6 hours.

The extracts thus obtained were filtered, placed in a continuous extractor, and extracted with benzene for 24 hours. This extraction removed any benzene-soluble tannin substances, part of some aminophenols and *m*-diamines, but none of the other organic bases. Saturated sodium carbonate solution (5 ml.) was added to the leather extract, which was then re-extracted with fresh benzene for a further 24 hours. Finally, the leather extract was made strongly alkaline by the addition of 2 ml. of 40 per cent. sodium hydroxide solution, and again extracted with fresh benzene for 24 hours.

Each benzene extract thus obtained was evaporated to dryness under reduced pressure, after the addition of 0·5 ml. of *N* hydrochloric acid. The residues were dissolved in water, and the solutions obtained were filtered, and tested by the methods previously described. The results are summarised in Tables II and III, which are arranged on a similar plan to Table I. Five mgrms. of a diamine or aminophenol had been applied to each of the leather samples, which all had the same area (2 ins. by 10 ins.).

TABLE II

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM SEMICHROME LEATHERS BY EXTRACTION WITH 1 PER CENT. ACETIC ACID

Diamine of aminophenol.	Leather. Weight. Grms.	Leather. Nature.	Benzene extract of acid extract of leather.	Benzene extract of acid extract of leather made alkaline with sodium carbonate.	Benzene extract of acid extract of leather made alkaline with sodium hydroxide.
			Positive reactions obtained:		
p-Phenylenediamine	8·2	Dyed	nil	*5*, 2, 4, 8 (0·10)	nil
m-Phenylenediamine	6·5	Dyed	—	nil	nil
,, ,,	7·7	Undyed	—	nil	nil
,, ,,	5·2	Undyed	1, 2 (trace)	—	—
m-Toluylenediamine	6·8	Undyed	nil	nil	nil
,, ,,	8·0	Dyed	nil	nil	nil
,, ,,	10·1	Dyed	nil	nil	nil
Metol	7·8	Undyed	nil	*4* (0·20)	nil
Amidol	6·2	Undyed	nil	nil	nil
o-Aminophenol	6·0	Undyed	1, 2, 6, *8* (0·20)	1, 4, *8* (0·20)	nil
m-Aminophenol	6·4	Undyed	*7* (0·06–0·10)	2, 4, 5, *7* (0·20)	nil
p-Aminophenol	5·8	Dyed	—	nil	nil
,,	6·0	Undyed	—	*4*, 6 (0·50)	nil

TABLE III

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM UNDYED SEMICHROME LEATHERS BY EXTRACTION WITH 0·1 *N* HYDROCHLORIC ACID

Diamine of aminophenol.	Weight of leather. Grms.	Weight of diamine or amino-phenol. Mgrms.	Benzene extract of acid extract of leather.	Benzene extract of acid extract of leather made alkaline with sodium carbonate.	Benzene extract of acid extract of leather made alkaline with sodium hydroxide.
			Positive reactions obtained:		
p-Phenylenediamine	6·0	5·0	Faint coloration* given by 2, 5, 7	2, 4, *5*, 7, 9 (2·0)	2, 4, *5*, 8 (0·10)
m-Phenylenediamine	6·1	6·5	Faint coloration given by 7	1, 2, *7* (0·60)	Possible trace by 7
m-Toluylenediamine	6·2	6·5	2, *7* (0·03–0·06)	2, *7* (0·12)	Possible trace by 7
Metol	6·4	5·0	Faint coloration given by 2, 7	*4*, 7 (2·5)	*4* (0·3)
Amidol	6·3	6·5	Faint coloration given by 2, 7	Possible trace by 2	nil
o-Aminophenol	6·7	5·0	nil	nil	nil
m-Aminophenol	6·6	5·5	*2*, 4, 5, 7 (0·3)	2, *7* (0·25)	nil
p-Aminophenol	6·5	5·5	Faint coloration given by 4	*4* (less than 0·05)	nil
Nil	6·8	nil	Faint coloration given by 2, 7	Faint coloration given by 2, 7	Faint coloration given by 2, 4

* "Faint colorations" were colorations which could not be matched by using very dilute solutions of the diamines and aminophenols in question.

From Table II it will be seen that, under the experimental conditions employed, *p*-phenylenediamine, metol, *o*-, *m*- and *p*-aminophenols are extracted from leather by 1 per cent. acetic acid. The *m*-diamines, however, are not readily extracted by this solvent; the results show that only a trace of *m*-phenylenediamine was extracted, whilst the amount of *m*-toluylenediamine extracted was so small that it could not be determined. As can be seen from Table III, 0·1 *N* hydrochloric acid extracts far larger amounts of these diamines, although, like acetic acid, it removes the *p*-diamine more readily than the *m*-diamines. Hydrochloric acid of the concentration employed is not such a good extracting agent for the *o*-aminophenol as 1 per cent. acetic acid.

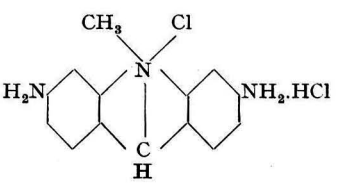
In conclusion, we wish to thank the Council of the British Leather Manufacturers' Research Association for permission to publish this paper.

LABORATORIES OF THE BRITISH LEATHER
MANUFACTURERS' RESEARCH ASSOCIATION.

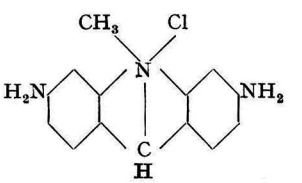
Note on the Recognition and Determination of the Flavines

BY P. J. UDALL, PH.D., A.I.C.

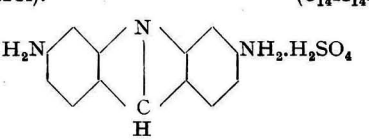
INTRODUCTION.—Since the discovery of acriflavine by Benda (*Ber.*, **1912**, **45**, 1787; *cf.* also Cassella & Co., D.R.P. 243085) this interesting compound, together with euflavine and proflavine, has been the subject of a considerable amount of research. The three "flavines" are all derivatives of diamino-acridine, and their antiseptic properties have been studied by many workers (*cf.*, for example, Browning and co-workers, *Brit. Med. J.*, 1917, 73; Browning and Gulbransen, *Proc. Roy. Soc.*, 1918, (A), **90**, 136; Bohland, *Deut. Med. Wochenschr.*, 1919, **45**, 797; Zell, *Amer. J. Vet. Med.*, 1920, **15**, 144; Lenz, *Z. ges. exp. Med.*, **12**, 195; Smith, *J. Pharm. Expt. Ther.*, 1923, **20**, 419), and it is obvious that the identification of these compounds, and their differentiation from other yellow dyestuffs, are of some importance when they are used for antiseptic dressings. They have the following constitutional formulae :



Acriflavine
($C_{14}H_{14}N_3Cl.HCl$).



Euflavine
($C_{14}H_{14}N_3Cl$).



Proflavine
($C_{13}H_{11}N_2.H_2SO_4$).

IDENTIFICATION OF THE PURE COMPOUNDS.—Tests have been carried out with the object of studying the effect of various reagents on the "flavines," and the results are tabulated below.

Reagent	Flavine		
	Acriflavine	Euflavine	Proflavine
	—	—	—
Concentrated sulphuric acid.	Green-yellow fluorescence. Evolution of HCl.	Green-yellow fluorescence. Evolution of HCl.	Green-yellow fluorescence.
Dilution of above solution.	Brilliant orange-red colour and fluorescence.	Brilliant orange-red colour and fluorescence.	Brilliant orange-red colour and precipitate.
Sodium hydroxide solution.	Yellow colour and precipitate. No fluorescence.	Yellow colour and precipitate. No fluorescence.	With excess reagent deposit of pale yellow needles.
Concentrated hydrochloric acid.	Reddish colour. No fluorescence.	Reddish colour. No fluorescence.	Reddish colour. No fluorescence.
Concentrated nitric acid.	Crimson lake colour.	Crimson lake colour.	Reddish colour. Slight fluorescence.
Dilute hydrochloric acid and potassium nitrite.	Violet colour.	Violet colour.	Violet colour.

To ascertain whether these "flavines," as a class, could readily be distinguished from common yellow dyestuffs of various types, the following dyes were subjected to the above tests:—Metanil Yellow; Paramine Khaki 20045; Dianol Fast Yellow ARX, Dianol Fast Orange D, Citronine Y conc., Titan Yellow G, Spirit Yellow 81451 and Eosin. Phenyl acridine, a substance of the same family as the "flavines," was also included. All the substances examined were readily distinguished from the "flavines" by the above reactions, from which it may be concluded that if, for any reason, a yellow dye not of the flavine type were used, there should be no great difficulty in detecting the substitution.

It will be seen that acriflavine and euflavine cannot be distinguished by these tests. Proflavine, however, may be recognised by its reaction with aqueous caustic soda, and also by the behaviour of its solution in strong sulphuric acid on dilution. Further, a definite precipitate is obtained with barium chloride solution—a reaction not given by either acriflavine or euflavine.

Acriflavine might be expected to yield a precipitate of silver chloride on treatment with silver nitrate in aqueous solution, but actually only a very faint turbidity is obtained, which cannot be looked upon as conclusive. It is stated in a recent paper (Howes, *Ind. Eng. Chem., Anal. Edit.*, 1930, **2**, 114) that acriflavine liberates carbon dioxide from saturated sodium bicarbonate solution. The reaction was found to be satisfactorily definite when solid acriflavine was used, but with aqueous solutions it was very difficult to detect evolution of gas.

To summarise these qualitative experiments, it will be seen that the "flavines" are readily distinguished from yellow dyestuffs of other types, and that proflavine gives certain characteristic reactions. Differentiation between euflavine and acriflavine would be desirable, and, since the qualitative reactions studied evidently

fail to distinguish between these very similar compounds, it was concluded that quantitative methods would have to be employed.

Various quantitative methods may be utilised to differentiate between acriflavine and euflavine in the pure state, *viz.* determination of carbon and hydrogen by the usual combustion method; determination of nitrogen; determination of amino group; determination of chlorine.

Kjeldahl's method may be used for the nitrogen determination. The amino group determination requires a more detailed explanation, as an external indicator must be used, and recognition of the end-point of the titration is a matter of some delicacy.

Standard potassium or sodium nitrite is prepared so that its strength is such that 1 c.c. = 0·01 grm. to 0·02 grm. of euflavine. Control experiments with pure euflavine have indicated that only one amino group takes part in the reaction. The standard nitrite solution is, therefore, prepared on this basis. The above limits to the strength of the solution are necessary, as it must be remembered that the "flavines" are used in very low concentrations, of the order of 1 in 500 and less. If the strength of the nitrite solution is outside the above-mentioned limits, either the amount of nitrite solution used will be very small, so that experimental error becomes proportionally large, or the end-point of the titration will be very indefinite.

A suitable weight of the flavine is dissolved in water (or a convenient volume of the liquid is taken, if a solution is under examination), excess of hydrochloric acid is added, the whole is cooled to 0° C. in a freezing mixture, and titrated with the standard nitrite solution, starch-iodide paper being used as indicator. The mixture must be constantly stirred throughout the titration. The end-point is reached when the bluish coloration (which is seen immediately after the liquid has soaked into the paper) persists for several seconds. Concordant results have been obtained by this method, when using 0·01 grm. of euflavine for each titration.

Identification of Antiseptic in Impregnated Dressings.—The determination of the nature of the antiseptic on a cotton fabric presents some difficulty. Usually the amount of the antiseptic is extremely small, and interference from impurities in the cotton may be serious.

The presence of a "flavine" on the fabric may be established by extracting the material with a suitable solvent (ethyl alcohol or water) in a large Soxhlet apparatus, removing the solvent, and subjecting the residue to the qualitative tests outlined above. Adulterants will readily be recognised; proflavine is detected by the reactions with barium chloride and caustic soda, but acriflavine and euflavine cannot be distinguished from one another. It would appear necessary, therefore, to have recourse to quantitative methods.

It is obvious that some material may be extracted from the cotton by the solvent used, and in practice this has been confirmed, cotton dressings impregnated with 0·1 per cent. of euflavine yielding extracts amounting to 0·2 to 0·4 per cent. If the extract be now subjected to quantitative investigation, difficulties arise. The combustion methods cannot be employed, owing to the impure state of the extract, which it appears impossible to purify from material extractable from the cotton.

The Kjeldahl method is suitable, provided that no nitrogenous matter is removed from the cotton by the solvent. Raw cotton contains a small amount of albuminous matter, usually equivalent to 0·3 to 0·7 per cent. of nitrogen. This is practically completely removed when the raw cotton is bleached, and purified cotton fibre consists of nearly pure cellulose (Knecht and Hall, *J. Soc. Dyers & Col.*, 1918, **34**, 220). One would not expect, therefore, to find an appreciable amount of nitrogen in highly-purified cotton to be used for medical dressings. As was to be expected, a blank determination, carried out on medical gauze, yielded no nitrogen.

In experiments with cotton gauze impregnated with euflavine, the nitrogen found corresponded with the amount of antiseptic on the fabric, two consecutive determinations giving identical results of 0·5 per cent. euflavine. It should be noted, however, that the result may be calculated as either euflavine or acriflavine.

Determinations of the chlorine content of extracts derived from impregnated dressings gave discordant results. As there is always a small amount of mineral matter present, even in highly purified cotton, it is possible that some chlorine is derived from this inorganic material. The amounts of chlorine in acriflavine and euflavine are 13·7 per cent. and 24 per cent., respectively, and it will be seen that a very small amount of inorganic chloride is sufficient to introduce a serious error when the chlorine is calculated as euflavine or acriflavine. Thus 0·056 per cent. of sodium chloride would be returned as 0·25 per cent. of euflavine, even though no euflavine had been added to the fabric. Mention should also be made of the fact that the "flavines" always contain a very small amount of mineral matter (Warren, *Repts. Lab. Amer. Med. Assoc.*, 1919, **12**, 64; 1921, **14**, 58). A determination of the amount of chlorine in a sample of pure acriflavine gave Cl = 24·4 per cent.; the formula $C_{14}H_{15}N_3Cl_2$ requires 24·0 per cent. of chlorine. This method, therefore, is not suitable when applied to impregnated dressings.

The method depending upon the determination of amino group may be applied to impregnated gauze, as there are no impurities present which affect the titration. The gauze is extracted with a solvent (ethyl alcohol has been found to be the most suitable) in a Soxhlet apparatus until the fabric is practically colourless, and, after evaporation, the residue is taken up with excess of dilute hydrochloric acid, warmed on the water-bath, with stirring, for about fifteen minutes and cooled to 0° C., and the titration is carried out as previously described. Concordant results may be obtained by this method; typical figures obtained, using gauzes containing 0·1 per cent. of euflavine, are as follows:—0·08, 0·09, 0·09, 0·10, 0·10 (mean 0·09) per cent. of euflavine.

In the course of the work described in this paper it was noticed that reactions appeared to take place when euflavine was treated with bromine or iodine. In the case of bromine, a brilliant red compound is formed, and it appears that six atoms of bromine replace six atoms of hydrogen in the euflavine molecule. This conclusion was drawn from the results of titration experiments, and I have worked out a quantitative method for the determination of euflavine or acriflavine, but the conditions are extremely rigid, and the method is not suitable for the rapid determination of euflavine. It is hoped to communicate these results in a further paper. The red compound has not yet been quantitatively examined, but its

reactions with certain reagents show a marked difference between euflavine and the brominated derivative.

Concentrated sulphuric acid.	Red coloration, becoming yellow on dilution.
Concentrated nitric acid.	Green coloration, becoming very pale orange on dilution.
Concentrated hydrochloric acid.	Yellow coloration.
Nitrous acid.	Yellow coloration, changing to dark red.
Hydrogen sulphide and ferric chloride.	Orange red coloration and precipitate.
Caustic soda solution.	Maroon coloration.

The reaction of euflavine with iodine is more complex, and a simple substance does not apparently result. Titration experiments indicate that four atoms of iodine react with one molecule of euflavine, yielding a brown-black substance.

SUMMARY.—1. The three "flavines" may be recognised and distinguished from other yellow compounds by the application of certain reagents, and proflavine may be readily distinguished by means of simple reactions.

2. Samples of "pure" acriflavine or euflavine can be differentiated by determining the percentage of carbon and hydrogen, nitrogen, chlorine or amino group.

3. Having limited the nature of the antiseptic on an impregnated gauze by qualitative methods, the amount can be determined accurately by means of the nitrogen or amino group methods, the results being expressible either as euflavine or acriflavine.

4. The amount of euflavine or acriflavine on an impregnated gauze cannot be found by determination of the amount of chlorine, owing to interference from impurities in the cotton.

5. Euflavine reacts with bromine and iodine; a red compound is formed, as a result of the reaction with bromine, and certain qualitative colour reactions of this compound are described.

I wish to thank Mr. W. L. Baillie, F.I.C., for his helpful advice.

DEPARTMENT OF THE WAR DEPARTMENT CHEMIST,
WOOLWICH, S.E.18.

Analyses of Two Samples of Irish "Bog Butter"

By P. S. ARUP, M.Sc., F.I.C.

THESE samples were found buried in the peat, one in Co. Leitrim, wrapped in a skin, and the other in Co. Tyrone, contained in a tub with perforated wooden handles. Such samples have been found, not only in Ireland, but also in Iceland and Finland. The analyses recorded here were undertaken, as there are not many modern data available in connection with this material, while the results offer some features of interest to the analyst concerned with butter analysis.*

Radcliffe and Maddocks (*J. Soc. Chem. Ind.*, 1907, **26**, 3) published the analyses of two samples of bog butter (one of which was due to Hart); figures from these analyses have been included in the Table below, for comparison.

The two samples which I have examined were grayish-white in colour, showing a few small specks of the original butter yellow in the interior. They were brittle and waxy, giving the impression of porosity, and smelled like rancid tallow. The specific gravity of the samples was 0·72; after melting, stirring and resolidifying,

* The desire to preserve the valuable nutritive constituents of milk in an edible form for use in seasons of scarcity can readily be understood, and different peoples appear to have solved the problem in different ways. Thus Marco Polo tells us of the dried milk of the Tartars, while from the writings of Pliny, Columella and other ancient authors, we gather that in their time cheese-making was already a highly-developed art among the Mediterranean peoples, while butter-making was practised by the Scythians and Germans, but not by the Southern peoples.

For purposes of preservation for any length of time, conversion into cheese is obviously a superior process to that of conversion into butter, and it is, therefore, not surprising to find that the custom of burying butter only persisted until comparatively recent times in those countries into which Mediterranean influence penetrated most slowly. The many difficulties attendant on the distribution of foodstuffs in former times undoubtedly enforced what must seem to us a considerable degree of tolerance of rancid and highly flavoured diet. There is even some evidence that a taste was developed for rancidity in butter; the Romans are said to have kept their butter until a certain degree of rancidity was produced; W. R. Wilde (*Proc. Royal Irish Academy*, 1856, **6**, 356) quotes as follows from Butler's *Hudibras*:

> "Butter to eat with their hog,
> Was seven years buried in a bog."

The archaeology of bog butter is dealt with in the above-mentioned paper, and in a communication to the *Irish Times* of May 16th, 1929, by Mr. Gogan, of the National Museum of Ireland, to whom I am indebted for the following information. A certain sample found in Tirnakill Bog, Co. Galway, was contained in a vessel dated 1789. It is probable that the practice of burying butter ceased in Ireland about the end of the eighteenth century, and that many of the specimens which have been found are of far greater antiquity, say, from the eleventh to the fourteenth century, the age of the older specimens being approximately determined by pyrographic decorations on the containing vessels. A certain estimate of age can also be deduced in some cases from the depth at which the specimen was found. No samples containing salt have ever been found.

From the large number of specimens found, some of which weigh as much as about 100 lbs., it would seem that the burying of butter must have been a widespread custom in Ireland.

the sp.gr. had increased to 0·84, showing that the material had contained gas, no doubt of bacterial origin. The analyses were as follows:

	Leitrim.	Tyrone.	Radcliffe and Maddocks.	Hart.
Water, per cent.	1·54	1·10	—	46·3
Curd, per cent.	1·31	1·64	1·97	0·32
"Casein" (from Kjeldahl result), per cent. ..	0·37	0·16	—	—
Ash, per cent.	0·10	0·29	—	—
Salt	nil	nil	nil	nil
Characteristics of fatty matter.				
Reichert–Meissl value	0·6	0·45	1·2	1·4
Polenske value	0·65	0·75	—	—
Iodine value	9·2	9·1	10·9	14·1
Acid value	190·7	196·9	201·9	—
Mean molecular weight of acids	294·2	284·9	—	—
Acetyl value	20·7	10·1	2·2	—
Melting point, °C.	45·6	47·9	48·0	44
Unsaponifiable matter, per cent.	0·65	0·58	—	—

The figures for "curd" represent non-fatty solids, and those for "casein" the nitrogen calculated as milk proteins (N multiplied by 6·39); they naturally do not represent these substances as ordinarily known; the very low "casein" in proportion to "curd" indicates loss of nitrogen. The high ash of the Tyrone sample is due to an abnormally high content of iron oxide, probably introduced by percolating water. Absence of salt seems to be a characteristic of all specimens of bog butter hitherto examined; it is not certain that they were made without salt, as this may have been removed by percolating water.

The fatty matter of the Leitrim and Tyrone samples had been completely hydrolysed to fatty acids. Fat hydrolysis in butter may be accomplished by two distinct groups of organisms, *i.e.* moulds belonging to the *Oidium*, *Penicillium* or *Cladosporium* orders, or by certain water bacteria, notably *B. fluorescens liquefaciens* or *B. prodigiosus*. The moulds consume part of the free fatty acids thus produced, notably the lower members, while the bacteria are eventually destroyed by the acids they liberate (Orla Jensen, *Dairy Bacteriology*, 1931, pp. 132 and 133, and Fierz David, *Z. angew. Chem.*, 1925, **1**, 6). In the case of small samples of butter, which expose relatively large surfaces to air, it is practically certain that the moulds will obtain predominance as typically aerobic organisms, which explains why hydrolysis is so often accompanied by a fall in the Reichert–Meissl value, as I showed to be the case with some old butter samples (ANALYST, 1929, **54**, 736), in which there was a certain quantitative parallel between the two processes.

In the four bog butters mentioned in the table, the soluble fatty acids had almost completely disappeared. This effect may have been largely due to the combined action of the fat-hydrolysing bacteria and the solvent action of percolating water, which would continuously remove excess of soluble acid and also introduce fresh bacteria.

The insoluble volatile (Polenske) acids were solid and powdery. They were probably largely derived from the oxidation of the unsaturated acids. Decidedly rancid butter fats often yield waxy solid insoluble volatile acids.

The low iodine values may be attributed to the chemical oxidation of the unsaturated fatty acids, as apart from the action of micro-organisms. A certain

diminution of this value may be expected in all fatty material which has been kept for a long time, unless excluded from oxygen; the present cases are, of course, of an extreme order.

The mean molecular weights of the acids are high, compared with the figures to be expected from the acids derived from fresh butter; for the Tyrone sample the figure approximates to the molecular weight of stearic acid (284·3), whilst for the Leitrim sample it is considerably higher. The disappearance of the lower acids is in itself not sufficient cause to explain this, and it is probable that hydroxy derivatives of the higher acids have been formed by oxidation. This supposition is supported by the fact that the acids from the Leitrim sample had the higher acetyl value.

From the unsaponifiable matter of both samples, characteristic crystals of cholesteryl acetate (m.pt., 115° C.), were obtained by the digitonin method, with one recrystallisation. The fact that the cholesterol has not been altered or consumed in these extremely old samples, indicates that, so far as this constituent is concerned, the phytosteryl acetate test may be relied on when applied to any such old samples as the analyst is likely to meet with.

I wish to thank Mr. R. Harvey, late Inspector under the Irish Land Commission, for presenting the samples for analysis, and the Department of Agriculture, Irish Free State, for permission to publish the results.

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The Antimony Trichloride Colour Test for Cod-Liver Oil

IN January, 1930, the Pharmacopoeia Commission appointed a Cod-liver Oil Colour Test Sub-Committee consisting of the following members:—J. H. Burn (Chairman), A. L. Bacharach, F. H. Carr, T. T. Cocking, N. Evers, H. A. D. Jowett, O. Rosenheim, and P. W. Tainsh.

The Sub-Committee was appointed to recommend a form of test for cod-liver oil, depending on what is known as the antimony trichloride reaction. In appointing the Sub-Committee, the Commission wished it to be understood that the inclusion of such a test in the Pharmacopoeia was not to be taken as necessarily indicating that the test afforded a measure of vitamin *A* content. The test, if included, might prove of value for indicating a limit of deterioration, or as indicating a characteristic property of cod-liver oil.

The Sub-Committee reported in March, 1931, and the Report was published by the Pharmacopoeia Commission. It was not found possible to include within the limits of this brief formal report to the Commission any account of the experimental work upon which the recommendations of the Sub-Committee were based. The following account is now published, in the hope that it will be of interest and value to other workers in this field.

Several modifications of the details of the antimony trichloride test, first proposed by Carr and Price, had been suggested from time to time, but no attempt had been made to show that, even by adherence to any one form of the test, the same results were yielded in the hands of different workers. The Sub-Committee set out to investigate the test, and to decide the conditions best calculated to give uniform results.

The Sub-Committee commenced their enquiry into the test by adopting, provisionally, conditions for its performance, based on the work of several workers, in general use at the time. They circulated the method and a number of samples of cod-liver oil to several chemists who had had considerable previous experience with the test. In some cases, these chemists arranged for additional observers in their laboratories to take readings for the purpose of comparison.

By proceeding in this way the Sub-Committee were at a great advantage over early investigators of the test, inasmuch as they were in a position to compare results obtained with the same sample of oil by a number of independent observers working under varying conditions.

The first results showed wide discrepancies. Three samples of oil ("A," "B," and "C"), distributed to four laboratories, showed the following variations:— "A," 6·5 to 10·1; "B," 4·5 to 6·1; "C," 9·7 to 15·2.

The necessity to investigate each stage of the test was, therefore, at once evident, and for the purpose two additional laboratories, with their staffs, were enlisted in the enquiry.

It became clear, after discussion, that the conditions for preparation of the antimony trichloride reagent, its concentration and method of storage, required closely defining if concordant results were to be obtained. The effects of variations in the reagent were carefully studied.

1. Effect of Concentration.—It was found that, with the same sample of oil and the same temperature for the test, a reduction in the concentration of the antimony trichloride reagent led to lower values being obtained; thus, at 20° C. the following table shows the results obtained with varying concentrations of antimony trichloride in B.P. chloroform:

Antimony trichloride, per cent.	29·0	26·9	25·1	23·1	21·0	19·0	17·0	15·1
Blue values	6·0	5·9	5·7	5·5	5·1	4·8	4·3	3·8

On the other hand, by carrying out observations at different temperatures, using, in each case, antimony trichloride solution, saturated at the respective temperatures of the tests, it was found that maximum and identical values resulted. The blue colour was, however, more fugitive and difficult to match when solutions of antimony trichloride of appreciably higher concentrations than 23·5 per cent. were employed.

2. Presence of Alcohol in the Chloroform used as Solvent of the Antimony Trichloride.—It was found that the presence of small percentages of alcohol in the chloroform employed as solvent of the antimony trichloride had a marked effect in increasing the solubility of the latter. In consequence, saturated solutions prepared by the different workers varied widely in strength, depending upon the alcohol content of the chloroform which they employed. The concentrations of antimony trichloride, saturated at 20° C. in pure dry chloroform

and in chloroform containing varying increasing amounts of alcohol, were found to be as follows:

Dry chloroform ..	23 per cent. w/v of antimony trichloride
With 1 per cent. of alcohol ..	38 „ „ „ „ „ „
„ 2 „ „ „ „ ..	50 „ „ „ „ „ „
„ 5 „ „ „ „ ..	80 „ „ „ „ „ „

Further, it was found that the presence of alcohol in the chloroform used for preparing the reagent had the effect of increasing the rate at which the colour faded, and thus added to the difficulties of ascertaining the maximum blue colour value. When, however, dry chloroform, free from alcohol, was used to prepare a solution of antimony trichloride saturated at 20° C., far more uniform results were obtained by all the workers for blue values, and also for the assay of the reagent by titration in verifying its content of antimony trichloride. Results of the assay of the reagent agreed closely, the mean figure of 25 determinations being 22·2 per cent. w/v of antimony trichloride, with extreme limits of 22·1 and 24·6 per cent.

Reagents prepared by the five workers were employed by each of them in testing two oils, and, except in the case of one worker, their results were in good agreement. For No. 1 oil the average of 20 observers was 6·2, with extreme limits of 5·5 and 6·9; and for No. 2 oil the average was 8·5, with extreme limits of 7·1 and 9·5.

Following the direction to use alcohol-free and dry chloroform in the preparation of the reagent, it was found by one worker that varying results were obtained by the use of chloroform which had undergone slight decomposition. Consequently, in the final details of the test, care was taken to prevent the use of decomposed chloroform by including the method of preparation of pure chloroform from the B.P. product. Although decomposition may take place in pure chloroform on storage, no indication was obtained of any deterioration occurring in the reagent over a reasonable period. The Sub-Committee ultimately recommended the following method for the preparation of the antimony trichloride reagent:

ANTIMONY TRICHLORIDE REAGENT.—A solution of antimony trichloride in pure dry chloroform, saturated at 20° C., is prepared in the following way:—Wash the chloroform two or three times with its own volume of distilled water, dry the chloroform over anhydrous potassium carbonate; pour off and distil, rejecting the first 10 per cent. of the distillate. During drying and distillation protect the chloroform from light. Wash antimony trichloride with the pure dry chloroform until the washings are clear. Prepare a solution, saturated at 20° C., of the washed antimony trichloride in the pure dry chloroform. The solution, which must contain not less than 21, and not more than 23 per cent. w/v of antimony trichloride, should be kept in a well-stoppered bottle of amber-coloured glass. *Assay.*—Mix 1 ml. with a solution of 2 grms. of sodium potassium tartrate in 20 ml. of water; rotate the mixture, add 2 grms. of sodium bicarbonate, and titrate with $N/10$ iodine. Each ml. of $N/10$ iodine is equivalent to 0·01141 grm. of antimony trichloride.

OTHER DETAILS OF THE TEST.—Having attained agreement regarding the reagent, the Sub-Committee then gave their attention to other details of the test.

It was found unnecessary to employ specially purified chloroform for preparing the solution of the oil for the test, since only 0·2 c.c. of this solution is required, whereas 2 c.c. of the reagent are directed to be used. Chloroform B.P. was, therefore, recommended for dissolving the oil, which was required to be weighed and not measured, thus ensuring greater precision.

Standardisation of Lovibond Glasses.—It was decided to measure the colour produced in the test through a colourless, rectangular glass cell of 10 mm. internal measurement, placed in a colorimeter designed for matching the colour of the solution, against colour glasses calibrated on the Lovibond scale. It was, therefore, considered desirable to check the uniformity of the standard blue glasses of a stated value of 5 units possessed by the different workers. For this purpose a specimen of the same blue glass was supplied to each worker for independent measurement against his glasses. The average of the mean values obtained by 30 observers was 4·93, and the mean figures of each observer differed from 4·93 by less than 0·1.

Source and Quality of Light.—The source and quality of the light used for illuminating the tintometer in the different laboratories were considered. The employment of "daylight" lamps was also investigated, but it was found that these varied so much in the quality of light emitted, even among lamps of the same brand, that it was not thought desirable to recommend them specifically for the particular purpose. It was agreed, however, that any source of light that would allow of an accuracy of reading within 0·1 unit might be used.

Effect of Method of Mixing.—The details of the technique to be adopted in adding the antimony trichloride reagent to the solution of oil were laid down, and it was decided not to specify any fixed interval before taking readings, as it was found that oils varied in their rate of colour development and subsequent fading. It was agreed that the value to be recorded was that corresponding to the maximum intensity of the blue component of the colour.

Effect of Dilution.—In order that the results by the different workers should be as comparable as possible with the different oils examined, it was required that the dilution of the oils should be such as to give an actual reading of close to 5 units. It was found that the majority of the observers showed the best agreement at about that value.

The necessity to employ red, yellow and neutral tint glasses in obtaining a colour match varied among the different observers.

The Influence of the Concentration of the Oil.—It has been shown by several observers that the graph relating the blue colour to the concentration of oil in the solution used for the test is not a straight line, but that the blue value diminishes with increasing concentration of the oil. This factor was, to some extent, responsible for the differences recorded between different observers in some of the earlier comparisons.

Since oils of widely different blue values cannot be compared in the same concentrations, because of the limited range within which it is possible to obtain accurate readings of the blue colour, it follows that any quantitative comparison of the blue values of such oils is fallacious.

Application of the Test to Unsaponifiable Matter.—The application of the test to the unsaponifiable matter, instead of directly to the oil itself, was considered by the Sub-Committee. A method was communicated to the Sub-Committee by Smith and Hazley, and subsequently published in THE ANALYST (**1931**, **56**, 265), by which the unsaponifiable matter could be readily prepared without loss of blue value. It has been shown (Church and Norris, *J. Biol. Chem.*, **1930**, **87**, 139) that when the test is so applied the graph relating the blue colour to the concentration of the oil is practically a straight line, and that the errors due to differences in concentration are thus avoided. It has also been shown (Coward *et al.*, *Biochem. J.*, **1931**, **25**, 1102; ANALYST, **1931**, **56**, 821) that the blue values obtained on the unsaponifiable matter show a better relationship to the biological values of the oils in vitamin *A*. It was decided, however, that, since the test to be recommended was merely a limit test, and since one fixed concentration of oil would be used in carrying out the test, the introduction of the further complication of preparing the unsaponifiable matter was not warranted.

Temperature.—In the earlier tests it was found that the colour was more permanent if the reading was taken at as low a temperature as possible, but, with the adoption of a solution of antimony trichloride saturated at 20° C., lower temperatures could not be used, as the reagent quickly becomes cloudy, even at a few degrees below 20° C. Moreover, there are practical difficulties in taking readings much below the temperature of the laboratory.

PHARMACOPOEIA COMMISSION,
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This test was introduced in 1926 by Carr and Price, who found that, with antimony trichloride in chloroform solution, vitamin *A* gives a blue coloration, which persists for several minutes, and may be matched against standard blue glasses in a Lovibond tintometer. The readings thus obtained on two samples of cod-liver oil were found to agree approximately with the contents of vitamin *A* in the samples, as determined by feeding experiments.

As a result of subsequent work by a large number of investigators, some difference of opinion exists as to the value of the test as an indicator of the vitamin *A* content of cod-liver oils. Consideration of the evidence available renders it probable, however, that, provided that the test is carried out under carefully specified conditions, rough parallelism exists between the results of the Carr-Price test and those of biological tests. At the same time, there seems no doubt that the blue colour obtained in the reaction with antimony chloride is the resultant of various colours which may be due to various constituents of the oil, and that these constituents may vary, at least as regards their proportions, in different samples of cod-liver oil. Moreover, the possibility of the presence in certain cod-liver oils of components which interfere with the coloration appears to have been proved by a number of independent investigations. It seems probable that a more satisfactory correlation between biological activity and the colour value of an oil may be obtained if the unsaponifiable fractions of the oils, instead of the oils themselves, are subjected to the test.

T. H. P.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

OILED WRAPS FOR APPLES

THE storage of apples in "gas" stores has now assumed importance, for each year the number of these stores increases. The main principles involved in this storage are that advantage is taken of the carbon dioxide evolved by apples, so that an atmosphere is created which contains a minimum of 10 per cent. of carbon dioxide, and a temperature of about 42° F. is maintained. When the concentration of carbon dioxide becomes excessive, the gas must be allowed to escape, but, in case of a leak apparatus is provided for the chemical production of carbon dioxide.

Heavy losses of apples so stored are apt to occur from "scald," unless the apples are enclosed in oiled wraps. These oiled wraps consist of paper squares,

impregnated with a medicinal paraffin, and they must not be confused with waxed wraps, for the latter are useless for wrapping gas-stored apples. The use of these wraps was first advocated in America, the discovery having been made, apparently, through the trial of a large number of substances. But the minimum amount of oil which these wraps should contain has never been determined, either experimentally or in practice, though the amount is invariably stated as 18 per cent. It is not quite clear whether the 18 per cent. alludes to the finished wraps, or whether 18 per cent. of oil should be added to the untreated paper. If 18 per cent. of oil is added to paper, the final paper should contain 15·2 per cent. I have examined several different consignments of American wraps, and I have found the amount of oil to vary from 11·5 to 14·9 per cent. These wraps have all been used with success. In their manufacture, oil is probably sprayed on to paper, and wraps in a consignment, or even in a package, show a considerable variation in oil content. If single sheets be examined from a package of about 300 wraps, a variation in oil content of about 1·5 per cent. may be found, but, if six one-half sheets of paper be taken, the variation is limited to about 0·5 per cent.

For the determination of oil, six one-half sheets of paper were usually extracted with petroleum spirit for two hours in a Soxhlet apparatus, after which the papers were air-dried, re-folded, and re-extracted for a further two hours. Similar figures are obtained if ether be substituted for petroleum spirit.

I have found the oil content of bundles of wraps to remain constant for three months, and I have little doubt that this constancy would be maintained for a much longer period, provided that no oil has exuded.

The rate of loss of oil, however, in wraps used for the wrapping of apples, or exposed to the air at ordinary temperatures, is somewhat remarkable, especially when the stability of the paraffin used is considered. Wraps were suspended by means of drawing-pins to wooden rods, and, after exposure to the air, were found to contain the following quantities of oil after the periods mentioned :

Original wraps Per Cent.	After 3 weeks' exposure Per Cent.	After 10 weeks' exposure Per Cent.	After 18 weeks' exposure Per Cent.
12·90	12·78	—	11·28
11·66	11·27	10·28	8·58
13·60	11·92	10·72	9·93

Oiled wraps may, therefore, lose considerably more than 3 per cent. of oil through exposure to air for a period of four months.

I have also examined oiled wraps actually used in the storage of apples in a "gas" store, and, from the results obtained, I have no doubt that considerable losses of oil occur. Therefore, the amount of oil found in used wraps must not necessarily be taken as representing the oil present in the original wraps.

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THE DETERMINATION OF ACTIVE CHLORINE

IN a well-known work on the examination of water it is suggested that if the starch iodide test is positive with a water slightly acidified, active chlorine may be sought for by means of the ortho-tolidine reagent, a yellow colour indicating its presence.

It must not be overlooked that a yellow colour is also produced by nitrite and ortho-tolidine, and by nitrite and benzidine. This appears to be due to the partial hydrolysis of the diazonium salt in dilute solution, a hydroxy compound being produced which couples with the undissociated diazonium salt. This takes

place feebly in acid solution, but, if the solution is made alkaline with soda or ammonia, the colour is greatly intensified.

We find that nitrite and active chlorine, in amounts usually present, may be distinguished by the fact that the starch iodide test does not give a positive result with nitrites in solutions less acid than *p*H 4, whilst active chlorine will produce a coloration in water with a reaction of *p*H 9.

Perhaps a more reliable method to follow is to test the water with *m*-phenylenediamine hydrochloride; if nitrites are present, active chlorine must be absent, since the two do not exist together. If nitrites are absent, the ortho-tolidine reagent may be used to determine active chlorine.

It may be noted that a distinct pink coloration is produced with *m*-phenylenediamine and active chlorine in concentrations exceeding 0·2 part per million.

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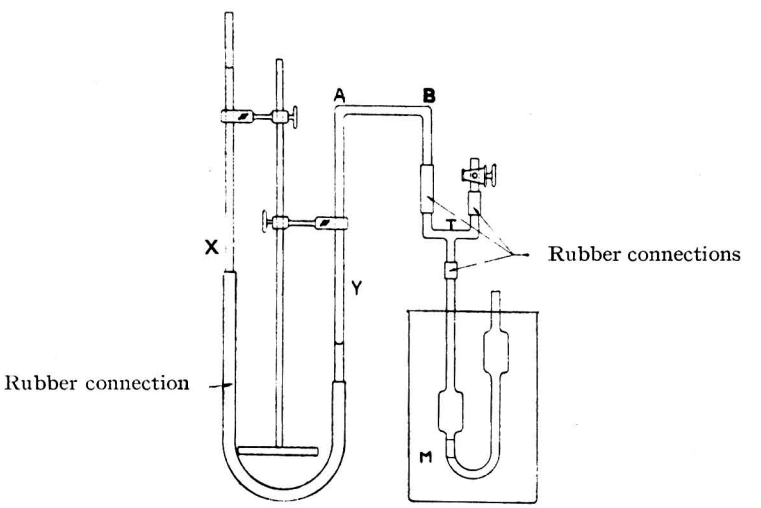
FILLING DEVICE FOR UPWARD-FLOW VISCOMETERS

The difficulty commonly experienced in filling upward-flow viscometers may be overcome simply and effectively by means of the apparatus shown in the diagram.

Y is a glass tube, bent at right angles at A, and again at B, and connected by a length of rubber tubing with a straight glass tube, X, which is supported by an adjustable clamp. Y also communicates with a T-piece (T), one limb of which is connected with the viscometer, and the other closed by a glass tap (or pinch-cock).



The liquid under examination is poured into the viscometer through the open limb (a drawn-out glass tube may conveniently be used for this purpose), and the liquid at M is controlled by adjusting the height of water (or other suitable liquid) in XY. Final adjustment is made when the liquid in the viscometer has attained the required temperature. This having been done, the glass tap (or pinch-cock) is opened, and the time of flow is noted in the usual manner.

This simple levelling device enables the final adjustment of the level of liquid in the viscometer to be made rapidly, and with a high degree of accuracy. It also eliminates the risk of fouling the walls of the viscometer above the lower reference mark (M).

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Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

BRITISH SHERRY AND THE PHARMACOPOEIA

On April 6th, an appeal was heard in the King's Bench Division (The Lord Chief Justice, Mr. Justice Avory and Mr. Justice Hawke) against the decision of Mr. Barrington Ward, who had dismissed a case against a grocer, for selling British sherry containing only 14·44 per cent. of ethyl hydroxide.

Mr. Roland Burrows, K.C., for the sampling officer, said that sherry ought to contain at least 16 per cent. of ethyl hydroxide by volume, as prescribed by the British Pharmacopoeia. The magistrate, however, had held that the Pharmacopoeia standard was applicable only to sherry intended for pharmaceutical purposes, and that it had not been proved that the purchaser had been prejudiced, since the wrapper on the bottle was transparent, and anyone could see that what was sold was British sherry, and that the analyst's certificate was not conclusive. Counsel submitted that the analyst's certificate was conclusive, and that what was sold was so deficient in one of the essentials of sherry that it could not be described as sherry.

The Lord Chief Justice said that no evidence was adduced to prove the nature, quality or substance of sherry in any sense other than that mentioned by the analyst. There was a case, relating to coffee and chicory, where the seller was held to be protected because the package described what was sold as a mixture of coffee and chicory, although that was only seen when the brown paper, in which it was wrapped up with other things, was taken off. But that did not apply to this case. The sherry was not sold as a mixture or labelled as a mixture. The bottle was labelled as British sherry. But the complaint was not that the sherry in the bottle, if there was any, was mixed with something else. The complaint was that the contents of the bottle were lacking in something essential to sherry. Here the utmost that could be said on behalf of the seller was that the label would have informed the purchaser, if he had seen it, that what he was getting was British sherry. But it was found, as a fact, that the purchaser did not see the label, though he might have done so. In these circumstances the magistrate ought to have convicted.

The other Justices agreed.

WHOLESALER'S SAMPLE

Twynham *v.* Badcock

On April 4th, the King's Bench Divisional Court, consisting of the Lord Chief Justice and Justices Avory and Hawke, allowed the appeal of an inspector under the Food and Drugs Act against the refusal of a magistrate to convict a wholesale dealer for selling ground ginger containing a preservative. The retailer of the ginger had been convicted, and proceedings were then taken against the wholesaler, but the magistrate had held that it was essential that there should be a fresh sample purchased from the wholesaler, and the sample divided and analysed.

Mr. Fox Andrewes, K.C., for the respondent, contended not only that a second sample was essential, but that there was no evidence on which the magistrate could find that his client wilfully sold the ginger knowing it to be adulterated. He relied on the invoice description.

The Lord Chief Justice, giving judgment, said that the allegation against the wholesaler was that he wilfully disobeyed the Act, because he took no steps to see that the ginger was free from preservative, but relied on the invoice description received from a vendor, who had had no analysis made for four years. It was impossible to say that there was no evidence on which the magistrate could find that the wholesaler was guilty of wilful neglect. The magistrate had refused to convict, because he thought that before there could be a conviction the same process of taking samples and having them analysed must be repeated. For this there was no warrant. The appeal would be allowed, and the case remitted to the magistrate, with a direction to convict.

The other Justices concurred.

New Zealand

SIXTY-FOURTH ANNUAL REPORT OF THE DOMINION LABORATORY

THE Annual Report of the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) for 1930 deals with the chemical analyses and investigations carried out on behalf of Government Departments. Of the 5541 samples examined, 3495 were received from the Health Department, and included 2486 samples of milk and 285 of human milk.

MILK.—The reductase test again proved its value for the detection of stale and insufficiently cooled milk. To comply with the Regulations, the milk must not completely decolorise the methylene blue in less than three hours. The Regulations also require that the test be applied within four hours of the procuring of the sample, and then only if the milk has been continuously kept in an ice-box from that time until the application of the test. Inspectors in the cities are provided with suitable ice-boxes.

The freezing-point test has been in constant use, and in no case has the freezing-point of genuine milk been found to vary appreciably from —0·55° C.

IODISED SALT.—Analyses of iodised salt were interesting. The standard in New Zealand is one part of potassium or sodium iodide to every 250 thousand parts of salt. Eight samples, examined in Dunedin, varied from one-third to two-and-a-half parts in 250 thousand. The iodide appeared to be unevenly distributed in the samples. In Wellington, one shipment was found to give irregular results, and five separate bags were examined. The middle portion of the salt in each bag had hardened, and portions from the surface and from the centre of the hardened salt were analysed. The results were:

Sodium iodide, parts per 250,000

	(1)	(2)	(3)	(4)	(5)
Surface ..	1·5	0·8	0·7	nil	0·3
Centre ..	3·2	1·1	1·2	nil	0·6

It will be seen that the iodide content was irregular, not only in the different bags of the shipment, but also in different portions of the same bag.

LIQUORS.—Under the Licensing Act it is an offence for a bottle which has contained liquor to be used again for liquor for sale, unless the label be destroyed. If re-bottling is suspected, a comparison is made with a genuine sample of the same brand, and, in the case of whisky, of the same vatting. Each distillery company furnishes a certificate that bottles bearing the same vat number have been filled with the same vatting. Determination of secondary constituents is sufficient to establish identity or difference, as the following example shows. The results are expressed in grm. per 100 litres of absolute alcohol:

	Suspected sample	Hennessey's Three Star Brandy
Fixed acidity	14·1	30·6
Volatile acidity	22·8	37·3
Compound ethers	39·3	80·1
Furfural	0·9	3·0
Extract (grms. per 100 c.c. of liquor) ..	0·86	0·57

The sample was evidently not genuine Three Star Brandy.

SODA WATER.—Of 18 samples of soda water examined, drawn from soda fountains, 13 contained appreciable amounts of lead, ranging from 1/20 to 1/3 grain per gallon. The lead was derived, in some cases, from lead piping, and in others from solder used in joints. Two samples contained iron (1/5 and 2/5 grain per gallon, respectively).

INCIDENCE OF GOITRE.—In the bulletin, "Goitre in School Children," by R. A. Shore and R. L. Andrew, published jointly by the Departments of Health and of Scientific and Industrial Research, the broad fact was established that where the iodine content of the soil was high, the incidence of goitre was low. In one district, however, both the iodine content of the soil and the incidence of goitre were low. Further work is being done on the iodine content of milk, eggs and vegetables from this district (also of human urine) in an attempt to solve the problem presented. The process for the determination of iodine in such material has also been investigated.

Siam

FIFTH REPORT OF THE GOVERNMENT LABORATORY

(FROM APRIL 1ST, 1928, TO MARCH 31, 1930)

IN his Report to the Ministry of Commerce and Communications, the Director of the Government Laboratory (Mr. A. Marcan, F.I.C.) states that the official work is tending to settle down on more definite lines, owing to the enactment of the Skimmed Milk Act and the Tariff Amendment Act, and to the more regular demands of the various Departments. The total number of samples examined was 6576, and various vegetable materials were also investigated.

THE SKIMMED MILK ACT, B.E. 2470.—In August, 1928, standards under this Act were published by the Department of Public Health, to come into force in February, 1929. The object of the Act was to prevent the importation of skimmed milk, which was being consumed in large quantities, with disastrous results to infants. The minimum standards are as follows:

Sterilised milk :	Fat,	3·25;	total	milk	solids,	11·75	per	cent.
Evaporated milk :	,,	3·78;	,,	,,	,,	25·5	,,	,,
Condensed milk :	,,	8·0;	,,	,,	,,	28·0	,,	,,

Of the 127 samples of milk submitted, 28 were found to be below the standards. The methods of analysis adopted were those of the Milk Products Sub-Committee of the Standing Committee on Uniformity of Analytical Methods (ANALYST, 1927, **52**, 402).

DRUGS FOR THE TREATMENT OF LEPROSY.—The following analytical values were obtained for the supplies of *Hydnocarpus anthelmintica* oil purchased, and the mixed ethyl esters produced therefrom:

	Acidity, per cent.	Sp.gr. at 30°/4° C.	Saponification value	Iodine value (Wijs)	Specific rotation $[\alpha]_D^{30}$	n_D^{30}
Oil ..	1·0–1·9	0·945–0·949	201·7–204·3	87·0–88·2	50·4–51·1	1·4740–1·4753
Esters	0·1–0·3	0·895–0·898	189·8–194·5	80·5–82·8	42·5–44·7	1·4531

Hydnocarpus ilicifolia Oil.—Three specimens gave the following results:

Acidity (as oleic acid) per cent.	Sp.gr. at 30°/4° C.	Saponification value	Iodine value (Wijs)	Specific rotation $[\alpha]_D^{30}$	n_D^{30}	M.pt. °C.
0·6	0·947	213·1	89·7	51·2	1·4763	23–28·2
21·0	0·944	203·6	89·7	52·7	1·4739	25·8–32·6
—	0·946	202·3	89·1	51·9	1·4749	—

Clinical trials with the sodium salts and esters of these oils were made, but, so far, the results have been indecisive.

MAHWENG.—The berries of this plant, *Solanum sanitwongsei*, have a local reputation as a remedy for diabetes. An investigation was made by the British Drug Houses, Ltd., but with entirely negative results. The fruit was found to contain no alkaloid, glucoside or guanidine derivative, and large doses of an extract administered to rabbits produced no change in the blood sugar. It was suggested that its reputation might be due to some relief in the subjective symptoms, but medical evidence is lacking, and it is apparent that the matter is not worth pursuing.

TOXICOLOGICAL EXAMINATIONS.—Of 77 exhibits examined, 25 were found to contain poisonous principles, *viz.* arsenic in 15, atropine in 5, croton seeds in water 1, and mercuric oxide, mercury, gelsemium alkaloid, and poisonous insects, 1 exhibit each.

Gelsemium alkaloid.—In this case the victim was supposed to have committed suicide by taking Chinese medicinal herbs, many of which are imported into Siam, but the vegetable material submitted did not match the herbarium specimen of *Gelsemium elegans*. In a Hong Kong case (ANALYST, 1930, **55**, 754) the alkaloid gelsemidine was isolated from the stomach contents of a young Chinese woman who had committed suicide.

Poisonous Insects.—Poisonous insects are newcomers in toxicological cases. The insects, known as maleng tao ba, were used in the preparation of a drug, and administered to a child of three for the cure of a rash, with fatal result. The insects were identified as a species of *Mylabris* of the *Cantharidae* family, no doubt containing cantharidin. They were stated to have come from China.

Poisoning by "Pak Wan."—Numerous cases of poisoning by "pak wan," the leaves of *Melientha suavis*, have been submitted, and attention is drawn to the matter in the hope that other laboratories have data or theories which might help to elucidate the problem. *Melientha suavis* (*Opiliaceae*) is a small tree, of fairly frequent occurrence, and the young leaf shoots are gathered and boiled and eaten as a vegetable. It is quite a common and popular dish, but it has the unexpected property of being poisonous at times. From the exhibits received, there is no

doubt that the leaves are "pak wan," and that no other tree has been mistaken for it. The usual symptoms are: giddiness and faintness, vomiting, collapse, and frequently death. Should the patient recover, a sore mouth is generally reported. From evidence collected it appears that the shoots of an individual tree may be consumed without ill results for years, but the time may come when they produce fatal results. No indication of the cause was apparent until it was observed that in a case in which death ensued, the tree from which the leaves were gathered had a number of abnormal shoots, and that many of these were infected by a small borer. It was not possible to identify this borer, but it was thought to be the larva of a moth. The evidence does not necessarily imply that the larvae are the cause of death, but the few observations which have been made do not lead to any other theory.

ANALYSES UNDER THE HARMFUL HABIT-FORMING DRUGS LAW.—Of 210 samples examined, 91 were found to contain active principles within the scope of the law. The presence of opium alkaloids in two drugs purporting to be cures for the opium habit is of interest.

The Relation Between Durability and Chemical Composition of Wood

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, AUSTRALIA*

THE comparatively early work on this subject (see Hawley and Wise, *The Chemistry of Wood*, New York, 1926) has indicated a relationship between the relatively few durable varieties of wood and their chemical compositions. In particular, it has been shown by Schmitz (*Idaho Forester*, 1922, p. 6), Hawley, Fleck and Richards (*J. Ind. Eng. Chem.*, 1924, **16**, 699), and by Sowder (*id.*, 1929, **21**, 981) that the relative resistance to destructive fungi may be determined in the laboratory from the toxicity of isolated aqueous extracts. This, however, is not in itself sufficient, since, for example, a certain constituent of an extract may be toxic to fungi, but not to termites (white ants) and *vice-versa*. A knowledge of the nature and specific function, if any, of each constituent of an extract is, therefore, of practical importance in connection with the preservation of timber.

In Australia, Baker and Smith (*A Research on the Pines of Australia*, Sydney, 1910; see also Cummins, Dadswell and Hill, *J. Council Sci. and Ind. Research, Australia*, 1930, **3**, 138) have examined the volatile oils from the various members of the cypress pine genus (*Callitris* spp.), the most durable, though rare, Australian wood. They obtained a crystalline and liquid fraction, *viz.* guajol and the so-called callitrol, respectively, and the latter was assumed, though on insufficient experimental evidence, to be toxic to termites. On the other hand, Oshima (*Proc. Pan-Pacific Science Congress, Australia*, 1923, p. 332) attributed the preservative power of oil from a Queensland cypress pine to the guajol, and found that high boiling-point fractions of camphor oil, which contained similar sesquiterpene alcohols, could be used successfully (and presumably economically) as preservatives.

In view of this conflicting evidence, and the scantiness of the information as to the nature of the extractives obtained with water and alcohol, I. W. and H. E. Dadswell carried out further tests on the relation between the durability and extractives of the cypress pines. Coarse sawdust or thin shavings from blocks, slabs

* Division of Forest Products. Reprint No. 4. By I. W. and H. E. Dadswell, Nov., 1931.

or logs of (so far as possible) the truewoods (*i.e.* the wood between the sapwood and the pith or heart) of *C. glauca, calcarata* and *intratropica* was treated as follows:—(1) Steam-distillation and extraction of the oil from the distillate by means of ether. (2) Extraction with 96 per cent. alcohol for 6 hours in a Soxhlet apparatus, the alcohol being then removed by evaporation, and the volatile oils separated as in (1).

In both cases phenols and acids were removed from the ethereal solution by extraction with 10 per cent. sodium hydroxide solution, guajol (white crystals, m.pt. 90° C., after recrystallisation from alcohol) being obtained as an insoluble residue. The sweet-smelling oils obtained from the alkaline mixture, before and after acidification, were then extracted with ether, and distilled under reduced pressure, the most important fraction in each case having the b.pt. 245° C. at 715 mm., and sp.gr. (15/15° C.) 0·9783. This fraction is probably the so-called callitrol of Baker and Smith, but, since uncompleted investigations by V. M. Trikojus indicate that it is an acid, the term *callitric acid* is proposed. Other fractions obtained were a liquid acid (b.pt. 150–156° C. at 18 mm.), and a viscous non-volatile oil (b.pt. 180–193° C. at 57 mm., *vide infra*).

(2*a*) Distillation of the ether-soluble portion of the semi-solid residue remaining after the removal of the volatile oils in process (2) yielded a dark green-blue oil (b.pt. 180–193° C. at 57 mm.), which set to a hard resinous mass. The insoluble portion, which, however, was slightly soluble in alcohol, was inorganic in character, and probably contained the manganese compounds which Baker and Smith (*loc. cit.*) record as characteristic of this genus.

(3) Extraction of 300 grms. of coarse sawdust for 3 hours with 3 litres of boiling distilled water, the filtered extract being concentrated to 200 c.c.

(4) Extraction by a similar procedure for 48 hours at 20° C.

YIELDS.—In general, samples of *C. glauca* and *calcarata* from New South Wales and Queensland, gave similar yields, whilst *C. intratropica* from Northern Territory (which was probably similar to that used by Oshima) contained almost twice as much material soluble in alcohol, and large amounts of volatile material containing guajol (for mean percentage yields, see Table).

Constituent (percentage yields)	*C. glauca*		*C. calcarata*		*C. intratropica*	
	Wood	Vol. oil	Wood	Vol. oil	Wood	Vol. oil
Steam distillation:						
Guajol	0·2	9·7	0·2	14·2	3·9	87
Sweet oil	0·5	21·5	0·5	30·7	—	—
Acids	1·2	50	0·8	55	0·6	15
Alcohol extract:						
Vol. in steam	2·3	—	1·4	—	4·0	—
Guajol	0·3	9·5	0·1	11·0	1·6	46
Sweet oil	0·6	17·1	0·5	40	1·7	42
Acids	1·8	54	0·6	46	0·5	12·3
Non-volatile in steam:	4·5	—	3·5	—	—	—
Ether-sol. resin in wood ..	3·8		2·4		—	
Do. in total extractives ..	56		50		—	
Ether-insol. resin in wood ..	0·7		1·1		—	
Do. in total extractives ..	9·7		22·1		—	
Soluble in alcohol	10·4		8·3		19·3	
Soluble in hot water ..	7·6		5·6		—	
Soluble in cold water ..	5·5		5·1		—	

Lower yields of volatile oils were obtained from sawdust that had been exposed.

TOXICITY TESTS.—(1) *Fomes annosus.*—Known dilutions of each constituent, diluted with sterile agar, were added to a culture medium containing 15 grms. of Merck's agar and 25 grms. of Saunders' malt extract in 1 litre of water, four 10 c.c. slopes being inoculated with mycelial flecks of this wood-destroying fungus, whilst uninoculated tubes and 4 inoculated tubes containing medium alone were used as controls; incubation was at 25–27° C. The tubes containing volatile oil were covered with waxed paper, placed over the plug, and in cases where no growth occurred during 4 weeks, the fungus was transferred to fresh medium to ascertain whether it had been killed.

Guajol had little effect on the growth of the fungus, and 1 per cent. of the sweet (*i.e.* unfractionated) oil had a retarding effect of 94 per cent., whilst 0·015 per cent. of the acids was toxic to the fungus; the resins had no effect, and were, in fact, "insoluble in the medium." A culture from a sample of rotten *C. glauca* gave similar results. Similar experiments with the aqueous extracts on the lines suggested by Hawley, Fleck and Richards (*loc. cit.*), showed retardations of 100 per cent. and 90 per cent., respectively, for 50 and 10 per cent. hot extracts of *C. glauca* or *calcarata*, and of 100 per cent. for both of the cold 50 per cent. extracts, but of only 50 per cent. for cold 10 per cent. extracts of *C. glauca*.

(2) *Termites.*—Sticks of *Pinus radiata* (4×1×0·25 inches) were dried at 105° C. for 2 hours, and immersed in solutions of the above constituents. The increase in weight, after slow evaporation at 20° C., was determined, and sticks immersed in alcohol alone served as controls. Field experiments, in which the sticks were placed in mounds of *Eutermes exitiosus* for a year, were unsuccessful, owing to the abundance of other food-material for the termites, and the effect on laboratory colonies made up of termite nest-material in stoppered glass jars was, therefore, tested. After 42 days there were signs of attack in wood treated with solutions containing 0·3 per cent. of guajol, 0·3 per cent. of sweet oil, 0·23 per cent. of non-volatile viscous oil or a saturated solution of ether-insoluble resin, and, after 192 days (during which the colonies were renewed 6 times), sticks treated with 1·4 per cent. of volatile acid and 1·9 per cent. of ether-soluble resin also showed signs of attack. It was not determined whether the dwindling of the colonies was due to natural causes or to the added materials. In view of the toxicity of the resin to termites, it is noteworthy that the wood of cypress pines contains no resin ducts and little wound tissue, the extraneous material responsible for their durability being located in the medullary ray cells and parenchyma.

These investigations suggest the possibility of treating wood with an appropriate preservative, which might be extracted from sawmill-waste or, possibly, synthesised. Future developments along these lines will, no doubt, be governed by economic considerations. J. G.

International Atomic Weights

SECOND REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

THE report covers investigations communicated to the Committee from February to October, 1931. The determination of the density of carbon dioxide at five different temperatures led to the value C=12·0054; similar measurements for sulphur dioxide gave S=32·059; and for methyl fluoride a figure nearer 19·01 than 19·00 for the atomic weight of fluorine. Comparison of the weights of specially purified krypton and oxygen by means of a micro-balance gave Kr=83·71; xenon was treated by the same method, and the higher value found by Aston (131·27) was confirmed (Xe=131·26 ± 0·005). The atomic weight of nitrogen

* By G. P. Baxter, Mme. P. Curie, P. Lebeau, O. Hönigschmid, and R. J. Meyer (*Ann. Chim. anal.*, 1932, **14**, 97–107).

was re-determined by means of the ratio $Ag:NH_3$, which, referred to the ratio $Ag:NO_3$ (very accurately known), allows of a calculation of $NO_3:NH_3$. The mean of eight of the most satisfactory determinations is N=14·0078 (Ag=107·879). The data of Hönigschmid on chlorine, now corrected for the solubility of silver chloride (0·0005 grm. per litre at 0° C.), lead to Cl=35·456[3]. Baxter, repeating the analysis of iodine pentoxide by thermal decomposition, found I=126·905, while Hönigschmid and Striebel arrive at 126·917 by determination of the ratio AgI:AgCl. The atomic weights of a number of elements, calculated by Aston on the basis of mass spectrographs, are included in the report. With regard to the discovery of isotopes of oxygen, the Committee fully agrees with Aston in not considering it advisable to depart from the present chemical basis O=16 for atomic weights, and for more refined physical measurements, also, the weight of the atom of oxygen 16 would be advisable. The changes introduced in the Atomic Weight Table for 1932 are:

Kr = 83·7 (older value 82·9)
Xe = 131·3 (,, ,, 130·2).

W. R. S.

Sale of Medicated Wines

RECOMMENDATIONS OF THE ROYAL COMMISSION*

THE Majority Report recommends that it should be possible to attach conditions to off-licences for druggists in the same way as can now be done for on-licences. Published recommendations of any kind of intoxicating liquor by a medical practitioner should be made illegal unless the full name, qualification and address of the practitioner are given with, and as part of, the testimonial. The various anomalies existing in the present law governing the sale of medicated wines and spirits are pointed out, and the need for bringing the licensing and excise law into harmony for both medicated spirits and wines is emphasised. A substitution of "medicines containing spirits" for the two terms "medicated spirits" and "spirits made up in medicine" is suggested, and their sale by duly qualified chemists or medical practitioners should continue to be exempt from the requirement of a justice's licence, and a corresponding exemption should be provided in revenue law. A more limited exemption, covering only those mixtures sufficiently medicated to be unfit for any beverage purpose, would be needed in those districts where there is no druggist's shop, and where such medicines (*e.g.* ammoniated tincture of quinine) are in frequent demand.

These should be labelled with directions as to dosage. The Commission regard it as possible to differentiate between "medicines rather than wines" and "wines rather than medicines." Such wines which can pass the test should be salable without justice's or excise licence, and be labelled as to dosage. Those not passing the test should be regarded as intoxicating liquors, and it should be an offence to describe them as "medicated."

The proposals as to sale of medicines containing spirits by others than druggists demand a test of medication, which should be the same for licensing and revenue purposes, and it is suggested that it be entrusted jointly to the Secretary of State and the Board of Customs and Excise or, on its appointment, the National Commission, to draw up and revise from time to time a list of spirits or wines sufficiently medicated to be incapable of use other than as a medicine or for medicinal purposes. The regularisation of the sale of absolute alcohol by chemists in quantities not exceeding 5 ozs., or of larger quantities on a doctor's prescription, is recommended, as is the exemption of perfumery and flavouring essences from the licences required for intoxicating liquors.

D. G. H.

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 4s. 6d.

(*Pharm. J.*, 1932, **128**, 42, 50–51.)

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Effect of Light on the Reduction of Methylene Blue in Milk. G. A. Aikins and A. C. Fay. (*J. Agric. Res.*, 1932, **44**, 85–95.)—The potentials of cream, whole milk, and skim milk drift towards the negative side when the liquids are exposed to sunlight. Potential changes, both to more positive and to more negative values, are deterred by the presence of fat, this influence being especially marked when the liquids are placed alternately in the sunlight and in the dark. Addition of fat to skim milk hastens the reduction of methylene blue in samples exposed to sunlight. Sodium oleate or stearate also shortens the time of the reduction, but, in this case, the cause is a more rapid fall of potential. The addition of methylene blue to skim milk or cream accentuates the changes in potential induced by sunlight. Various observations made confirm Whitehead's conclusion that reduction of methylene blue by light is a reaction distinct from that induced by bacteria (ANALYST, 1930, **55**, 594).

As the solution develops a progressively more negative potential, the methylene blue is decolorised whenever such potential passes through the zone of reduction characteristic of this dye. Similarly, the blue colour re-appears when the solution develops a potential sufficiently positive to oxidise the dye present. When skim milk, containing methylene blue which has been reduced by sunlight, is placed in the dark, the potential quickly becomes positive enough to re-oxidise the dye. Artificial light (electric) appreciably hastens the reduction of methylene blue in commercial milk. T. H. P.

Phosphorus Content of Casein, R. E. L. Berggren. (*J. Biol. Chem.*, 1932, **95**, 451–460.)—The amount of phosphorus in casein has been a matter of some dispute, and it was, therefore, decided to make a further study of this subject. An attempt was first made to determine whether the amount of phosphorus in the casein is influenced by the quantity of phosphate in the milk from which it is prepared. Caseins were prepared in different ways from four portions of cow's milk. Their phosphorus contents were determined by the Fiske–Subbarow colorimetric method, and nitrogen by the Kjeldahl method. The two caseins which had been precipitated in the presence of a large excess of phosphates, had higher ratios of phosphorus to nitrogen than did the two caseins which had been prepared from milks the phosphate content of which had been reduced by dialysis. That this difference was not due merely to standing was shown by the fact that casein prepared from milk which had been kept in the refrigerator until it soured, had a slightly higher phosphorus to nitrogen ratio. Further study of the phosphorus content of caseins prepared from dialysed milks has shown that it is a relatively simple matter to prepare caseins of much lower phosphorus contents than have previously been reported for caseins obtained directly by acidification of milk. The rate of dialysis was very slightly increased by the use of a Simms dialyser. Chloroform and toluene were found to be superior to thymol in preserving the milk.

It was found that when milk was acidified, then dialysed, with chloroform as the antiseptic, the loss of total nitrogen on dialysis was the same as that for milk containing chloroform but no added acid, but the rate of loss of phosphorus on dialysis was much more rapid. The lowest value obtained for any casein was 0·29 per cent. of phosphorus, assuming that this casein contained practically the same amount of nitrogen as casein prepared from undialysed milk, namely, about 15·46 per cent. This casein was prepared from milk which had been preserved with chloroform and dialysed for 36 days before the casein was precipitated. It has not hitherto been possible to separate directly from milk caseins of such low phosphorus content. There is nothing to indicate that this low value is the minimum phosphorus content of casein. It is possible that the fractions of the mixture of proteins in milk, called "casein," contain different amounts of phosphorus, and lose phosphorus at different rates on dialysis of the milk, and that the phosphorus is much more loosely bound in the casein than has been previously supposed. Further work will be necessary to determine whether or not the loss of phosphorus from casein on dialysis of the milk is purely chemical in nature, or whether it is caused by the action of enzymes or of bacteria, or is brought about by some combination of these processes. P. H. P.

Determination of Phosphorus in Casein. R. E. L. Berggren. (*J. Biol. Chem.*, 1932, **95**, 461–464.)—In the course of an investigation on the phosphorus content of casein it became necessary to find a method, for the determination of phosphorus, which would require only small amounts of casein, and yet be sufficiently accurate for the work. The colorimetric method of Fiske and Subbarow (*J. Biol. Chem.*, 1925, **66**, 375; ANALYST, 1926, **51**, 205) has been found to be extremely suitable for this purpose. The results obtained agree well with those found gravimetrically. The method is much more rapid than those commonly employed, and only 10 or 15 mgrms. of casein are required for a determination. An average of the results obtained with nine different casein preparations gave 0·80 per cent. of phosphorus by the colorimetric method, and 0·805 per cent. by the gravimetric method. The method described in the "Report of the Association of Official Agricultural Chemists" (Washington, 2nd edition, 1925), in which the phosphorus is weighed in the form of magnesium pyrophosphate, was the gravimetric method used for comparison. P. H. P.

Rancidity Reactions of Fats. P. Bruère and A. Fourmont. (*Ann. Falsif.*, 1932, **25**, 94–97.)—*Reactions depending on iodides.—Bulir's reaction* consists in dissolving 1 grm. of fat in 10 c.c. of petroleum spirit, and adding 2 c.c. of a 20 per cent. solution of potassium iodide in 90 per cent. alcohol, followed by 15 c.c. of water. After shaking, starch is added, and a blue coloration indicates rancidity. *Lea's test* depends on heating an acetic acid and chloroform solution of fat with potassium iodide in an atmosphere of nitrogen, cooling, diluting with potassium iodide solution, and titrating with 0·02 *N* thiosulphate solution.

Taffel and Revis's Reaction.—A simplified method, which is recommended, is to dissolve 5 grms. of the fat in a cold mixture of 20 c.c. of acetic acid, 25 c.c. of 95 per cent. alcohol, and chloroform to make up to 100 c.c. One grm. of finely-powdered potassium iodide is added, the mixture is shaken, and, after 30 minutes'

contact, with occasional shaking, 50 c.c. of water are poured in; the mixture is shaken, and the solution is titrated with 0·2 *N* sodium thiosulphate solution, with or without starch. By making many comparative tests with the Kreis reaction and the Vintilesco and Popescu reaction, it is concluded that if 1 c.c. of 0·2 *N* iodine is liberated by 1 grm. of fat, the fat may be regarded as rancid. D. G. H.

Nature of Antioxygens present in Natural Fats. I. Separation of Fatty Derivatives from "Antioxygens" by Distillation. T. P. Hilditch and J. J. Sleightholme. (*J. Soc. Chem. Ind.*, 1932, **51**, 39–44T.)—The capacity for oxygen absorption of olive, tung, and codling oils (at 100° C.), and of linseed oil at 70° C., has been examined; also that of their corresponding mixed fatty acids and methyl esters before and after distillation, and, in some cases, that of the glycerides re-synthesised from their distilled fatty acids. A modification of Thomas's hydrogenation apparatus was used (*J. Soc. Chem. Ind.*, 1920, **39**, 10T), and observations of the rate of absorption of oxygen were made at suitable intervals. An induction period preceding steady absorption was clearly marked in each of the original oils; it consisted of two periods, one of negligible absorption, and a succeeding interval during which absorption increases more or less slowly. Maximum rapidity was rarely attained before 50 c.c. of oxygen had been absorbed by 10 grms. of oil. The induction period was much reduced by saponification of the fats and liberation of the mixed acids, but was restored very slightly when the acids were esterified. Distillation of acids or esters led to a further decline in the period, and maximum rates of absorption afterwards were of much the same order for any particular oil and its corresponding mixed acids or esters, whether distilled or not. The shortest induction periods in the respective series were for glycerides prepared synthetically from the distilled acids of olive or linseed oils. Five fractions of increasing boiling point and iodine value were prepared by distilling the mixed esters of olive and linseed oils *in vacuo*, and the induction period in these series was found greatest in the fractions of low boiling point, and at a minimum in the penultimate fractions consisting almost wholly of unsaturated esters of the C_{18} acids. Results are considered to confirm the view that natural anti-oxygenic compounds accompany the original fatty oils, and cause the "induction periods" on exposure to the action of oxygen. These may not all be of the same type, and proteins or their degradation products may possess such properties. Preliminary experiments with olive oil show that the induction period is almost eliminated on boiling the oil with dilute hydrochloric acid or giving a very mild treatment with insufficient caustic alkali to effect appreciable hydrolysis. Shaking with concentrated sulphuric acid yielded an oil more resistant to the action of oxygen than the original. D. G. H.

Detection of Bilberry Juice in Red Wine. W. Diemair. (*Chem. Ztg.*, 1932, **56**, 247.)—The filtrate obtained after decolorisation of wine by heating it for a short period with charcoal, probably contains some of the original colouring matter in the form of a "colourless isomer," since the colour may be partly re-generated by the action of concentrated hydrochloric acid at the boiling point. In this way a slight yellow-red colour was obtained from red wine, whilst bilberry wine, alone or in admixture with red wine, showed a colour change through blue,

green-blue and blue-violet to yellow-brown. These reactions, which are due to the presence of oenidin dimethyl ester and myrtillidin monomethyl ester, respectively, may be used to detect adulteration (*cf.* Ofner, ANALYST, 1931, **56**, 672).

J. G.

Determination of Ammonia, Trimethylamine, and other Amines in Foodstuffs. F. Okoloff. (*Z. Unters. Lebensm.*, 1932, **63**, 129–154.)—The literature on these determinations is reviewed critically, and, as the result of experiments on the distillation of amine and ammonia mixtures, and on the behaviour of the distillates towards formaldehyde and nitrous acid, the following methods of determination are proposed:—*Ammonia in the presence of Primary Amines.*—Three hundred c.c. of liquid containing an artificial mixture of ammonium sulphate with methylamine (or with herring-extract), are distilled with magnesium oxide into an excess of standard sulphuric acid, and the distillate is evaporated to 75 c.c., and, when cool, titrated with alkali until faintly red to phenolphthalein. The colour is then discharged by 1 drop of 0·1 *N* acid, and the liquid is evaporated to dryness on the water-bath, 30 c.c. of alcohol being added at the last stages. The dry residue is cooled in a desiccator, and extracted for 1 minute with one 40-c.c. and two 30-c.c. portions of 96 per cent. alcohol, the extract being filtered into one flask, whilst the solid residue is extracted with warm water, and this extract filtered into another flask. Formol titration by the usual method (*vide infra*) is then applied to both solutions (after dilution, in the former case, with 200 c.c. of cold boiled water). The amine nitrogen and ammoniacal nitrogen are obtained, respectively, from the alcoholic and water extracts with figures ranging from 102 to 105 per cent., in the presence of 4 to 9 and of 20 mgrms. (as *N*) of the respective compounds. *Trimethylamine in the presence of Methylamine and Ammonia.*—Two 300-c.c. portions of herring-extract, to one of which a known amount of trimethylamine had been added, were used. The solutions are distilled into excess of 0·1 *N* acid, and the distillate, after 15 minutes at the boiling-point, is cooled and titrated in the presence of 0·2 c.c. of a 0·2 per cent. solution of rosolic acid, in order to obtain the total volatile bases. The neutral liquid is then boiled for 40 minutes with 15 grms. of sodium nitrite and 25 grms. of glacial acetic acid, in a total volume of 300 c.c., in order to decompose any methylamine into nitrogen and methyl alcohol, and three-quarters of the volume of the resulting liquid is then distilled in the presence of 50 c.c. of 30 per cent. sodium hydroxide solution into an excess of 0·1 *N* acid. If carbon dioxide is removed from the distillate by boiling, and the excess of acid in the cool liquid is titrated in presence of rosolic acid, the factor 1·4 gives the trimethylamine nitrogen. The accuracy in the presence of 3 to 17 mgrms. of total nitrogen, and 3 to 13 mgrms. of trimethylamine nitrogen is about 95 to 104 per cent. for both compounds. *Ammoniacal Nitrogen and Amino Nitrogen in Herrings.*—The viscera and bones are removed, and 50 grms. of the minced flesh are extracted for 24 hours in the ice-chest with 1 litre of water, the mixture being then shaken well and, after 30 minutes, strained through a sieve. The extract is then divided into two 400-c.c. portions, and treated as described above, in order to obtain (*a*) the total volatile nitrogen, and (*b*) the trimethylamine nitrogen, while (*c*) the ammoniacal nitrogen is determined in one of the distillates

(neutral to rosolic acid) by titration with 0·2 *N* alkali, after addition of 20 c.c. of clear formalin. The accuracy of formol titration for the determination of ammonia was shown to be affected by the presence of 5 to 10 mgrms. of a primary amine, though not by secondary amines, rosolic acid being preferable as indicator in the presence of 5 to 25 c.c. of trimethylamine (accuracy 99 to 106 per cent. for 2 to 10 mgrms. of ammoniacal nitrogen). In the absence of trimethylamine, neutral red, litmus, phenolphthalein or rosolic acid solutions have an accuracy of 97 to 101 per cent. for 1 to 50 mgrms. of ammoniacal nitrogen; methyl red is unsuitable. Tests on 39 samples of herrings showed a positive Eber's test reaction in 28 cases, and ammoniacal nitrogen, trimethylamine nitrogen, and other volatile nitrogen contents of 1 to 181, 0 to 18, and 0 to 13 mgrms. per 100 grms. of herring, respectively. J. G.

Occurrence and Detection of Choline in Coffee. F. E. Nottbohm and F. Mayer. (*Z. Unters. Lebensm.*, 1932, **63**, 176–182.)—It has been shown (*id.*, 1932, **63**, 47) that certain difficulties in the determination of trigonelline in coffee extracts are associated with extracts containing large amounts of sugars. A similar cause is now suggested as an explanation of previous failures to find choline in coffee extracts, and the autoclave method, suggested by the authors for the determination of trigonelline, has been applied to this end. The trigonelline chloride is, therefore, removed, as already described (*loc. cit.*, and ANALYST, 1931, **56**, 405, 543), and the clear filtrate is evaporated until free from alcohol, and is then diluted to 50 c.c. with hot water, after which the sugars are destroyed by the action of 10 c.c. of hydrochloric acid (sp.gr. 1·124) in an autoclave at 4·5 atmospheres. The resulting solution is warmed with animal charcoal, and then filtered and evaporated to a syrup, the cool mass being extracted with 40 c.c. of absolute alcohol. The alcohol is removed from the clear extract, and a solution of the residue, in 25 c.c. of water and 3 c.c. of hydrochloric acid, is again treated with animal charcoal, the solution being evaporated in a vacuum, and the residue then extracted 3 times with 5 c.c. of absolute alcohol. The choline is finally precipitated from a solution in 25 c.c. of water and 2 c.c. of acid, by addition of 10 to 15 c.c. of a 20 per cent. solution of phosphotungstic acid in water. It is filtered off, and washed with 5 per cent. hydrochloric acid, and is then decomposed by addition of a cold saturated solution of barium hydroxide. After removal of the barium phosphotungstate, the filtrate is acidified and evaporated at a low pressure. The residue is extracted twice with 7 c.c. of cold absolute alcohol, and the residue, after evaporation and drying over sulphuric acid, is ready for the determination of choline (*cf.* Roman, *Biochem. Z.*, 1930, **219**, 218). It is, therefore, dissolved in 10 c.c. of water, and 1 c.c. of this solution is mixed with 0·3 c.c. of a solution containing 157 grms. of iodine and 200 grms. of potassium iodide per litre. After 30 minutes at 0° C., the dark-brown needles of the choline-iodine compound are separated by filtration, and are washed with 5 c.c. of ice-water, and a solution of the residue in 10 c.c. of absolute alcohol is then titrated with 0·1 *N* sodium thiosulphate solution by the procedure described for trigonelline (*loc. cit.*); 1 c.c. ≡ 1·335 mgrms. of choline. Santos coffee (250 grms.) contained 0·022 per cent. Choline compounds:—$C_5H_{14}NOCl,AuCl_3$, golden needles or prisms, soluble

in water, dilute hydrochloric acid, or alcohol, m.pt. 245 to 249° C., with decomposition; $C_5H_{14}NOCl,PtCl_4$, orange prisms or plates, soluble in water or dilute alcohol, m.pt. 233 to 234° C., with decomposition; $C_5H_{14}NOCl,6HgCl_2$, colourless hygroscopic prisms or needles, soluble in water or 96 per cent. alcohol, m.pt. 240 to 243° C. J. G.

Determination of the Saccharin Content of Foodstuffs and Beverages, and particularly of Beer. J. E. Heesterman. (*Chem. Weekblad*, 1932, **29**, 130–134.)—The present work is based on the method of Lerrigo and Williams (ANALYST, 1927, **52**, 377), though it is considered that this method is unsuitable for beer on account of the impure nature of the final residue, and of the difficulty of obtaining its ammonium content by a direct colorimetric method. Detailed investigations of the individual stages of the method resulted in the following optimum working conditions:—Normally, 50 c.c. of beer and 5 c.c. of 4 *N* hydrochloric acid are shaken with 100 c.c. of a mixture containing equal volumes of petroleum spirit (b.pt. 40 to 60° C.) and ether. The extract is evaporated until less than 50 c.c. remain, and this residue is transferred with a little solvent to a 50 c.c. flat-bottomed flask, and evaporated to dryness. The residue is heated with 10 c.c. of 3 *N* hydrochloric acid for 1½ hours under a reflux condenser (a diagram of a convenient micro-form is given), and 10 c.c. of 4 *N* potassium hydroxide solution are then added to the cool mixture. The ammonia is removed by distillation, at the rate of about 3 c.c. in 5 minutes, through a tube, bent so as to avoid contamination of the distillate by priming, into a test-tube cooled in water. In this way most of the ammonia is obtained in the first few c.c., and may be titrated with 0·001 *N* hydrochloric acid in the presence of 2 drops of a 0·02 per cent. solution of methyl red (previously adjusted, by addition of 0·1 *N* hydrochloric acid, until red in colour). The resulting solution is then diluted until about 0·00005 *N* to ammonia, and matched by Nessler's method against a suitable standard containing ammonium sulphate. The usual precautions for obtaining ammonia-free reagents, water and apparatus are indicated, but allowance should, nevertheless, be made for any blank obtained by a repetition of the whole process without the beer. The method was tested on 21 varied samples of beer containing 0 to 200 mgrms. of the crystalline sodium derivative of saccharin ($+2H_2O$) per litre, and was found to be sensitive to 5 mgrms. per litre. A more refined process, sensitive to 1 mgrm. per litre, is also described, in which 150 c.c. of beer and 15 c.c. of acid are extracted with 300 c.c. of the solvent mixture, the extract being then shaken with 40 c.c. of *N* potassium hydroxide solution, and washed with 10 c.c. of water. The alkaline liquors, which contain all the saccharin, are acidified with 5 c.c. of hydrochloric acid (sp.gr. 1·19), and, after a further extraction with the solvent mixture, the procedure already described is followed. In general, titration gave results a few mgrms. per litre higher than the colorimetric method. J. G.

New Reactions of Salts of Quinine. Volumetric Method for Determining the Alkaloid. M. J. Papavassiliou and J. Georgiadès. (*J. Pharm. Chim.*, 1932, **124**, 167–177.)—To the known precipitants of quinine may be added palladium chloride. If to a 1 per cent. solution of palladium chloride a few drops

of a neutral quinine solution are added, a yellowish amorphous precipitate, insoluble in alcohol and soluble in acids, is formed. Oxidising substances modify the precipitate. In the presence of chlorine water a flocculent yellowish precipitate forms, and as little as 0·001 grm. of quinine in solution may be detected. The precipitate, if allowed to form slowly from a hot solution, forms very small, fine, colourless crystals of characteristic form. With hydrogen peroxide the precipitated crystals are similar, but reddish. In the presence of 5 per cent. chromic acid and an equal volume of 1 per cent. palladium chloride, an amorphous bright yellow precipitate is formed, soluble in boiling water, sparingly soluble in alcohol, and insoluble in ether and chloroform, and the reaction is capable of detecting 1 part of quinine in 6000. With cinchonidine, cinchonine and quinidine similar precipitates are formed; with papaverine a microscopically distinct yellowish precipitate; with solanine a yellow powdery precipitate; and with brucine and strychnine yellow precipitates, turning reddish-brown. The strychnine precipitate is entirely crystalline, and may readily be distinguished under the microscope from that of quinine. In the presence of sulphuric acid, quinine reduces alkaline chromates and dichromates, as is the case with cinchonidine, quinidine, aconitine, pilocarpine, and colchicine. The reduction of potassium permanganate forms a convenient method of determining quinine. The quinine sulphate (0·1 grm.) is dissolved in 100 c.c. of water; 10 c.c. of (1:3) sulphuric acid are added, and the mixture is heated at 50 to 60° C., after which 50 c.c. of 0·1 *N* potassium permanganate solution are run in, the whole carefully mixed, and 0·5 grm. of oxalic acid added. The liquid is then titrated with 0·1 *N* potassium permanganate solution until a faint pink colour persists for a few seconds. After reduction, the liquid shows a characteristic fluorescence. D: G. H.

Biochemical

Assimilation of Aluminium by the Human System. S. Judd Lewis. (*Biochem. J.*, 1931, **25**, 2162–2167.)—A spectrographic method was employed for determining aluminium in blood and in milk: the material was evaporated, and the residue gently ignited until free from carbon; the ash was transferred to the lower electrode of an arc-lamp, and the spectrum observed in the usual way, by means of a large Hilger quartz spectrograph, the intensity of the two principal aluminium lines giving a measure of the aluminium present. The lines could be recognised with certainty when the concentration of aluminium was one part in 10 millions. It was found that normal blood usually contains no aluminium, and when it does contain any, the proportion is very small, 0·3 part per million being the highest value recorded. Aluminium, in amounts ranging from nil to 1·3 part per million (in one case 5 parts), was found in the blood of persons who had included a meal of scones containing 94 mgrms. of aluminium (the form in which the aluminium was present is not stated) in their normal daily diet. Aluminium was not detectable in the blood until 4 to 5 hours after the special meal; the maximum quantity found remained constant during the period over which special meals were taken. Milk (human, cow's, and goat's) was found normally to contain either *nil* or, at the most, in the case of cow's milk, 0·3 part per million of

aluminium; an increase of a fraction of one part per million in the aluminium content was detected in most of the samples taken several hours after the subject had been given a dose of alum. S. G. C.

Determination of Sugars in Plant Extracts. T. G. Phillips. (*J. Biol. Chem.*, 1932, **95**, 735–742.)—In order to be able to make a satisfactory choice among the methods available for the determination of sugars in plant extracts, and to make the best possible interpretation of the results obtained, it seemed necessary to study the following points:—(1) The comparative action of a number of oxidising reagents on a variety of plant materials. (2) The behaviour of these reagents toward sucrose hydrolysed by invertase. (3) The most reliable method for the calculation of sucrose hydrolysed by invertase when determined in the presence of reducing sugars. The results obtained by the use of four oxidising solutions, including three differing degrees of alkalinity, are now reported. The solutions are Fehling's solution, the micro-reagent of Shaffer and Hartmann (*J. Biol. Chem.*, 1920, **45**, 365), Tompsett's reagent (*Biochem. J.*, 1930, **24**, 1148) and a bicarbonate solution. It is shown that no one of the four oxidising reagents is best for all the plant extracts used. It is probably safe to assume that the reagent giving the lowest amount of sugar in a given extract has determined all the true sugars present, and that the excessive values obtained by the other methods are due to non-sugars to which these reagents are sensitive. So far as the materials studied are indicative, it appears that a choice may be made by comparing Fehling's solution and the bicarbonate reagent. Comparison with the Shaffer–Hartmann reagent is suggested, as, because of its convenience, it is preferred for use with extracts to which it can be applied. As used in the study, Fehling's solution is not reliable for the determination of amounts of glucose less than 5 mgrms. It may be used to determine as little as 2 mgrms. of sucrose in the presence of 5 mgrms. or more of glucose. The calculations of sucrose determined in the presence of reducing sugars must be made in a manner suited to the peculiarities of the oxidising reagent used. P. H. P.

New Colour Test for Cysteine. E. Dyer and O. Baudisch. (*J. Biol. Chem.*, 1932, **95**, 483–489.)—The highly distinctive naphthoquinone test for cysteine, important for the detection and determination of sulphur-containing amino acids, requires the presence of three free groups in the molecule, namely, –SH, $-NH_2$ and –COOH, a fact which partly explains its remarkable specificity. A similar unusual degree of specificity has now been observed in the reaction of *o*-benzoquinone with cysteine. When an aqueous solution of cysteine hydrochloride is shaken with a chloroform solution of *o*-benzoquinone a deep red colour is produced in the chloroform layer. The test appears to be a specific qualitative reaction for cysteine; the chemistry of the colour reaction has not yet been studied in detail. To prepare the *o*-benzoquinone a mixture of 0·4 grm. of catechol, 1·5 grm. of anhydrous sodium sulphate, 1·5 grm. of silver oxide, and 10 c.c. of dry ether was shaken in a test-tube for 35 seconds, then filtered at once. The ethereal filtrate, chilled in a freezing mixture, deposited red crystals of the quinone, which were separated by decantation, washed once with 1 to 2 c.c. of ether, and dissolved in 8 c.c. of chloroform. Two c.c. of the freshly-prepared solution were

used for each test. When 2 c.c. of an aqueous solution of cysteine hydrochloride which contained 0·001 grm. of cysteine per c.c., were added to 2 c.c. of the chloroform solution of the quinone, and the mixture shaken vigorously, the pleochromatic colour of the chloroform layer was first discharged, giving a pale yellow. On further shaking for about 2 minutes a deep red colour was developed in the chloroform layer. The aqueous layer gradually became pink on prolonged standing, owing to decomposition of the quinone itself. The test was always made in a neutral or weakly acid medium. The red cysteine-quinone-chloroform mixture is immediately decolorised by reducing agents, such as sodium sulphite solution, sodium cyanide solution, or hydrogen sulphide, and is slowly decolorised when shaken with an oxidising agent, such as perhydrol. Cysteine cannot be detected by the *o*-quinone test in concentrations smaller than 10 parts per million. With high concentrations of cysteine a large excess of quinone is necessary for production of the characteristic colour. No other amino acids and sulphur-containing compounds so far investigated have given the colour, and it is shown that the reaction may be used to detect cysteine in the presence of cystine, glutathione, and many other sulphur and nitrogen compounds. The sensitivity of the test is lessened by the presence of relatively large quantities of glutathione, but is unaltered by the presence or absence of alanine. The effect of various solvents for the *o*-quinone was tried, but chloroform was found to be most suitable. It is shown that the test is also applicable to cystine by reduction to cysteine; the limit of sensitivity of this test is 100 parts of cystine per million. P. H. P.

Serum Diagnosis in the Investigation of Foodstuffs. C. Griebel and H. Maass. (*Z. Unters. Lebensm.*, 1932, **63**, 166–176.)—Uhlenhut's precipitin test may be applied to the detection of extracts of certain seeds which are not easily distinguishable by microscopic or chemical methods. The procedure is to remove the fat from the finely-ground seeds by extraction with ether, the sugars and free plant-acids then being extracted with 70 per cent. alcohol, and the residue dried in a desiccator. It is next extracted with physiological salt solution at room temperature or in the incubator, and 2 to 5 c.c. of the filtered liquid are injected 6 to 12 times into the auricular veins of dogs at intervals of 2 to 4 days. The serum is then withdrawn and tested in dilutions of 1:200 to 1:3,000 by the usual Uhlenhut method, observations being made in all cases after 20 minutes; 0·1 c.c. of normal dog-serum +1 c.c. of antigen, and 0·1 c.c. of antiserum + 1 c.c. of physiological salt solution should be used as controls. Sera obtained from extracts of both almond and apricot stones reacted towards both of these, but were not sufficiently specific to distinguish these stones from one another; attempts to distinguish the resulting precipitates by fractional precipitation, or by other methods, also failed. The serum from walnuts did not give a reliable specific reaction for this seed, but specific sera were obtained from pine seeds and from cashew (anacardium), hazel nuts and arachis nuts. It was possible in this way to detect small amounts of these nuts when present as foreign ingredients in marzipan or persipan; almonds, hazels, arachis nuts, and walnuts, were also detectable in chocolate. An anti-serum prepared from plasmon, and diluted to 1:2,000, was used to detect 1 per cent. or more of plasmon in the binding substance of sausages. J. G.

Preparation of Crystallised Anti-Beri-beri Vitamin from Yeast. R. Tschesche. (*Chem. Ztg.*, 1932, **56**, 166–167.)—The known reactions of vitamin *B*1 have been confirmed, and certain new reactions ascertained. On the basis of this information, a number of methods of separating the vitamin, resulting finally in a pure product, have been developed. The procedure employed consisted mainly in adsorption of autolysed brewery yeast on fuller's earth, precipitation of foreign substances with silver nitrate, mercuric sulphate and lead acetate, and application of Seidell's benzoylation process. In this way 100 c.c. of extract, corresponding with 50 kilos. of yeast, were obtained. Treatment of this extract, with gold chloride or picrolonic acid gave an amorphous precipitate, and when this was filtered off, the filtrate yielded crystals of the vitamin aurichloride or picrolonate within a few hours. After crystallisation of the picrolonate from water and conversion into the hydrochloride, 70–80 mgrms. of crystalline product were obtained (from 100 kilos. of yeast). These crystals contain both nitrogen and sulphur, and the free base has the probable formula $C_{12}H_{17}ON_3S$. By its sulphur content, vitamin *B*1 resembles insulin and glutathione. The compound is optically inactive, and in ultra-violet light it shows an absorption maximum at 250 to 260 mμ, as was found by Guha and Damianovich for vitamin *B*1 preparations made from yeast.

The results of a large number of tests give for the pigeon-unit the value 2·4γ. The crystals are thus the most active material yet obtained, and the fact that the activity is not changed by conversion of the hydrochloride into the gold salt or picrolonate and back to the hydrochloride, indicates the material to be pure vitamin *B*1. A sample of Jansen and Donath's preparation, made from rice, and supplied by these authors, was also found to contain sulphur, so that the formula $C_6H_{10}ON_2 + HCl$ is inaccurate. The mixed melting-points of the two hydrochlorides showed no depression. The sulphur present is moderately labile, and is split off by cold potassium permanganate solution, or by concentrated nitric or sulphuric acid, and when the compound is boiled with barium hydroxide solution hydrogen sulphide is evolved. T. H. P.

Lovibond Values of the Liver-Oils of various Animals, and Growth Promotion of different Vitamin Preparations. P. Karrer, H. v. Euler and K. Schöpp. (*Helv. Chim. Acta*, 1932, **15**, 493–495.)—For the liver-oils of a number of animals, birds, and fishes, which had mostly died from disease, the Lovibond values for the reaction with antimony chloride have been determined. High values are shown for the liver-oils of various fish, *e.g.* sole (350), salmon (143), *Hippoglossus hippoglossus* (200), *Scombresox saurus* (500), turbot (800), and *Stereolepsis ischinagi* (about 3000). Among birds, the cormorant, which feeds largely or wholly on fish rich in vitamin *A*, gives the value 0; the same is the case with the seal. The liver-oil of the hen, after feeding on grass and carotene, shows the value 400–500, or, after normal feeding, 75. Of the mammals, the pure carnivora (lion, tiger) give zero values, the bear traces, and the zebra 53. Among reptiles, *Coluber quadrilineatus* shows the value 0, *Lacerta ocellata* 200, and *Basilicus americanus* 400. The amphibian, *Amblystoma*, gives the value 0.

Biological tests on a number of vitamin *A* and vitamin *A* ester preparations

gave the following results, the cod-liver oil values (C.L.O.) being calculated from the formula, (20 × blue value) ÷ (mgrms. of substance per c.c.):

	C.L.O.	Daily dose	Increase in weight per day
Vitamin *A* from *Scombresox saurus*, regenerated from the *p*-nitrobenzoate	8000	1·2γ	0·45 grm.
Vitamin *A* stearate from *Scombresox saurus*	3000	4	0·5
Vitamin *A* acetate ,, ,, ,,	7000	2	0·7
Vitamin *A* from *Hippoglossus hippoglossus*	8800	1	0·4
Vitamin *A* from the turbot	9800	0·5	0·9
,, ,, ,, ,, ...	9800	0·3	0·55
After fractional adsorption on kaolin of the part of *H. hippoglossus* vitamin *A* not adsorbed by the adsorbent ..	8000	1	0·8
,, ,, ,, ,,	8000	0·5	0·5

T. H. P.

Application of the Carr-Price Reaction to Carotinoids. B. v. Euler and P. Karrer. (*Helv. Chim. Acta*, 1932, **15**, 496–502.)—The reagent used was prepared by saturating washed, dried and distilled chloroform at 20° C. with antimony chloride, which had been previously dried and washed with chloroform. Into 0·2 c.c. of the chloroform solution of the substance to be tested, 2 c.c. of an antimony chloride solution of definite concentration was run from a micro-burette, the colour being then determined in a 10 mm. layer of the liquid in a Lovibond tintometer. The measurements were made by the two authors in Stockholm and Zurich, respectively.

The results thus obtained with a number of different carotinoids vary with the time of the reaction, the mode of mixing, etc., and are apparently influenced to some extent by the conditions of illumination of the apparatus. If the blue coloration attains its maximum intensity within the first three minutes, it is suitable for use in calculating the C.L.O.-value. The accuracy of the above procedure, as applied to carotinoids, is estimated at about 10 per cent. T. H. P.

Action of Selenious Anhydride on Sterols. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51**, 144.)—A red precipitate of selenium, or a red coloration, is obtained when a solution of ergosterol in 95 per cent. alcohol is boiled with 3 to 4 c.c. of aqueous selenious anhydride solution. With a few mgrms. of ergosterol in 5 c.c. of the alcohol, the reaction is detectable after 1 to 2 minutes' boiling. The minimum amount of ergosterol detectable is about 0·0006 grm. Derivatives of ergosterol, *e.g.* γ-dihydroergosterol acetate, also give the reaction, but with diminished intensity. Other sterols, such as chemically pure cholesterol, stigmasterol and the phytosterols, give negative results. Irradiation of ergosterol is accompanied by progressive diminution in the intensity of the reaction, owing to the formation of the yellow resin resulting from the destruction of the irradiated ergosterol or vitamin *D*. T. H. P.

Quantitative Determination of Alpha-dihydroergosterol in Ergosterol from Ergot. M. C. Hart and H. Emerson. (*J. Amer. Chem. Soc.*, 1932, **54**, 1077–1078.)—A typical ergosterol preparation was analysed by first fractionally

separating 100 grms. into 4 crops of crystals and a final mother liquor, and finding the specific rotation of each fraction. From these values, and on the assumption that a mixture of ergosterol ($[\alpha]_D = -132°$) and α-dihydroergosterol ($[\alpha]_D = -20{\cdot}4°$), was being dealt with, the composition was calculated, and not less than 30 per cent. of α-dihydroergosterol was found. A third sterol, in minute quantity, was possibly present. D. G. H.

Purification of Benzidine, and an Improved Reagent for Determination of Haemoglobin in Blood. F. C. Bing. (*J. Biol. Chem.*, 1932, **95**, 387–388.)—In the quantitative determination of haemoglobin, by the method of Bing and Baker (*J. Biol. Chem.*, 1931, **92**, 589), a very good grade of benzidine is essential, and many samples, including expensive products, have been found unsatisfactory, even after purification, as recommended. By means of the following method of purification, a suitable reagent was obtained from all the samples of benzidine that were tried. The method depends upon the fact that the interfering substances in most commercial specimens of benzidine are soluble in 50 per cent. alcohol. Twenty grms. of benzidine base are dissolved in 200 c.c. of ordinary ethyl alcohol, with gentle heating, and filtered to remove insoluble material. The filtrate, after the addition of 1 grm. of blood charcoal (extracted with hydrochloric acid and re-activated), is stirred, and kept at a temperature of 50° C. ± 10° C. for 15 minutes. This can best be done on an electric hot plate. While warm, it is filtered, and the charcoal is washed with 10 c.c. of warm alcohol. The treatment with charcoal is repeated until the filtrate is almost colourless. Two to three additions of charcoal are usually sufficient, but with highly coloured products ten to twelve treatments may be necessary. To the filtrate 135 c.c. of distilled water are added, or sufficient water to make the alcohol 50 to 60 per cent. by volume, and the whole is warmed, if necessary, to obtain a clear solution, and then left in the refrigerator for 24 to 48 hours to crystallise the benzidine. The crystals are dried by suction on a Buchner funnel, washed with cold 50 per cent. alcohol, dried by continued suction, and preserved in a bottle protected from light. From 20 grms. of a highly coloured technical product 12 grms. of purified material were obtained. All benzidine so prepared has given a negative result when tested as follows:—With the aid of heat, 1 grm. of purified benzidine is dissolved in 20 c.c. of glacial acetic acid, and 30 c.c. of distilled water, and 50 c.c. of ordinary 95 per cent. alcohol are added. This constitutes the reagent now used in the haemoglobin determinations. The solution may have a trace of yellow colour, but decolorisation with charcoal at this stage is not desirable. In a test tube are placed 2 c.c. of the reagent, 1 c.c. of distilled water, and 1 c.c. of 0·6 per cent. hydrogen peroxide, and mixed. No coloration, or only a very slight yellow tint, should develop in 2 hours. If this mixture is diluted to 25 c.c. with 20 per cent. acetic acid, and viewed through a thickness of about 1 cm., it should be practically indistinguishable from distilled water. The new reagent gives, with blood, exactly the same amount of colour as the old one, even though the concentration of benzidine is halved. For haemoglobin determinations the technique of Bing and Baker is followed, except that 2 hours are allowed for full colour development. The reaction mixture may, if desired, be allowed to stand for several hours before dilution to 25 c.c.

P. H. P.

Toxicological

Presence of Lead in the Herbage and Soil of Lands Adjoining Coke-Ovens and the Illness and Poisoning of Stock Fed Thereon. J. T. Dunn and H. C. L. Bloxam. (*J. Soc. Chem. Ind.*, 1932, **51**, 100–102T.)—The examination of soil and herbage in the vicinities of several coke-oven works in different districts showed that lead, manganese and copper were present in considerable proportions. The investigation was the outcome of the mysterious deaths of cattle and sheep. In the case of a sheep, the kidneys contained 1·7 part per million of lead, and 2·1 parts of copper; manganese, 0; the liver (part only), 2·6 parts of lead, 3·5 parts of copper, and no manganese; the stomach tissue, 0·6 part of lead, 3·2 parts of copper, and 8·3 parts of manganese; stomach contents, 0·2 part of lead, 1·8 part of copper, and 7·2 parts of manganese. The stomach and intestines of a dead bullock from the same farm contained 0·8 part of lead per million; 1·0 part of copper, and 97·0 parts of manganese. Soil, sub-soil (2 ft. below the surface), and grass in fields on this farm contained, respectively, in field A, lead 1·1, 0·4, 14·1; copper, 17, 3 and 4·7; manganese, 43, 158 and none; field B, soil, grass and turf near road, lead, 5·5, 11·5, 2·2; copper, 24·4, 4·2 and 26·7; manganese, 84, none and 74; field C, lead 1·1, copper 8·7, and manganese 14 parts per million, whilst for fields in other industrial districts figures were considerably higher.

Experiments so arranged as to exclude the possibility of the metals being derived from wind-blown soil or dust are now in progress, to confirm the inference that lead and copper are being introduced at the present time. Samples of soil, herbage, and grass, from purely agricultural districts, in no case contained lead or copper, and it is evident that any industrial process involving consumption of large quantities of coal might emit lead and copper compounds in sufficient quantity to poison neighbouring pastures. D. G. H.

Organic Analysis

Highly Sensitive Reagent for Hydrazines and Analogous Compounds. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51**, 127.)—When heated with selenious anhydride solution (4 per cent.), hydrazine, phenylhydrazine, etc., give a red precipitate of selenium. When 5 c.c. of the reagent are used, 0·00025 grm. of phenylhydrazine, 0·0001 grm. of semicarbazide hydrochloride, or 0·001 grm. of phenylsemicarbazide is detectable in this way. Inversely, when two or three drops of phenylhydrazine are dissolved in 10 c.c. of water acidified with hydrochloric acid, and the solution is heated with selenious anhydride solution, about 0·0003 grm. of selenium is detectable by the formation of the red precipitate. (*Cf.* ANALYST, 1930, **55**, 294.) T. H. P.

New General Reagent for the Enolic Form. E. V. Zappi. (*Bull. Soc. Chim.*, **1932**, **51**, 54–59.)—Compounds with free enolic modifications, that is, containing the group ·C(OH):CH· in the molecule, such as acetylacetone, ethyl acetoacetate, or ethyl malonate, reduce mercurous nitrate solution with formation of very finely divided mercury, the extent of the reaction being apparently proportional to the concentration of the enols in the solution. Compounds existing

in the pseudo-forms, imino-alcohol [·C(OH):N·], thio-imino-alcohol [·C(SH):N·], isonitrile (:C:NH), iso-cyano- (O:C:N·) and isothiocyano-compounds, and isonitro-compounds [:C:N(OH):O], effect similar reduction. The same is the case with compounds containing active unsaturated linkings of the allyl (R·CH_2·CH:CH· or R·CH_2·CH:CHR) or acetylene type (CHR:CHR). Theobromine, with enolic structure, responds to this reaction, whereas caffeine, in which the only labile hydrogen is replaced by a methyl group, does not react. Camphor, which contains in its molecule the enolisable group ·CO·CH_2·, also gives a negative result, but it has been found that the enolic structure is assumed only when the camphor is dissolved in sodium ethoxide, or is in presence of Grignard reagent. As a test for enolic compounds, mercurous nitrate is far more satisfactory than ferric chloride, which is by no means specific.

The reagent is prepared by treating 50 grms. of mercury with 50 grms. of nitric acid (sp.gr. 1·2) in a porcelain dish, separating the resulting crystals after the lapse of 24 hours, and dissolving them in 5 parts of boiled distilled water containing 10 per cent. of nitric acid. It is stored in presence of a small amount of mercury.

The compound to be tested is dissolved in 4 to 5 times its volume of alcohol, and the solution then treated with its own volume of the reagent. With much free enolic modification, the grey precipitate of mercury forms immediately; otherwise the liquid requires short boiling (usually less than 30 seconds). If necessary, other solvents without action on mercurous nitrate, such as water, ethyl or amyl esters, petroleum spirit, glycerol, or chloroform, may be used, miscibility of the solvent with the aqueous reagent being unnecessary. T. H. P.

Fractionation of American Gum Spirits of Turpentine and Evaluation of its Pinene Content by Optical Means. S. Palkin. (*U.S. Dept. Agric., Tech. Bull. No.* 276, Jan. 1932.)—American gum-spirit of turpentine is obtained, almost exclusively, from the species *Pinus palustris* (longleaf) and *caribaea* (slash pine), and, like that from *P. maritima*, is composed mainly of the isomers α-pinene and nopinene (or β-pinene), the quantities and proportions of which are of commercial importance in the synthesis of camphor and in the manufacture of terpin hydrate. With the possible exception of ozonisation, no quantitative chemical method exists for the differentiation of these isomers, but Darmois, Dupont and others (*Chim. et Ind.*, 1922, **8**, 549, 553, 555; *Bull. Soc. Chim.*, 1923, **33**, 1252; *Bull. Inst. du Pin*, 1929, **60**, 155; **65**, 269) have effected separation, to some extent, by efficient fractional distillation, the proportions of the isomers in the mixtures also obtained being calculated from the rotatory dispersions by the Biot relationship. The present author describes an improved, electrically-heated assembly, comprising a plate rectifying-column with a pressure-regulator and dephlegmator condenser, which was used successfully for the fractionation of turpentine in a vacuum. Fixed pressures (20 and 65 mm.) were used, so that the temperatures of distillation were reasonably accurate indications of approximation of a pure component. The proportions of the isomers in the fractions were determined from the equation X_1 (proportion of α-pinene) $=(a_0-a_2)/(a_1-a_2)$, where a_0 is the rotation of the fraction, and a_1 and a_2 are the rotations of pure α- and β-pinene,

respectively. Similarly, beyond the point at which pure β-pinene is obtained, $X_2=(a_0-a_3)/(a_2-a_3)$ where X_2 is the proportion of β-pinene having the rotation a_2, the rotation of the dominant tailings-constituent being a_3. Since differences in density are negligible, actual and not specific rotations may be used. The results shown in the table do not indicate that the increasing use of slash pine as a

Source and sample	Rotation (10-cm. tube) a_j (=578mμ)	Rotation (10-cm. tube) a_v (=546mμ)	$n_D^{25°}$	$d^{15·6°}$	Composition α-pinene Per Cent.	Composition β-pinene Per Cent.	Composition Tailings Per Cent.
Commercial, from mixed fields of slash and longleaf pine:							
1	− 2·4°	− 2·2°	1·4697	0·8707	63·0	31·5	5·6
2	− 9·2	− 9·98	1·4692	0·8662	61·9	32·6	5·3
3	1·9	2·5	1·4680	0·8664	62·2	28·8	6·1
4	− 1·58	−12·58	1·4701	0·8692	59·2	36·9	3·9
Samples from authentic sources:							
Slash pine 3, old	−20·50	−22·56	1·4698 1·4663	0·8667 0·8624	58·0	35·6	6·4
Longleaf pine 1, fresh	14·04	16·27	1·4691	0·8680	68·4	28·6	3·0
Longleaf pine 2, fresh	12·29	14·34	1·4692	0·8694	62·5	33·3	4·2
Gum dip 8, slash	−22·58	−24·9	1·4694	0·8657	61·0	33·7	5·3
Gum dip 9, longleaf	11·0	12·86	1·4690	0·8667	62·5	34·4	3·1
Scrape 10, slash	−25·05	−27·8	1·4700	0·8704	58·8	33·6	7·6
Scrape 11, longleaf	7·35	8·85	1·4681	0·8675	67·0	29·2	3·8

source of American turpentine will tend to diminish its β-pinene content, the increase of turpentine having a negative rotation, being due, probably, to the nature of the α-pinene, and not to any material change in the proportions of the isomers. No material differences in the total contents of α- and β-pinene were noted, and differences in proportion cannot be ascribed to the variety or to the dip or scrape form of the pine. J. G.

Empirical Classification of Vat Dyestuffs. C. M. Whittaker. (*J. Soc. Chem. Ind.*, 1932, **51**, 66T.)—The use of 21- and 36-filament 150 denier viscose yarn enables a classification of vat dye-stuffs to be made. Knittings containing 150/21 and 150/36 denier yarns are dyed with the respective dye-stuffs at 20°, 30°, 40°, 50°, and 60° C. Sufficient dye-stuff for five dyeings is vatted at 60° C. with the requisite quantity of sodium hydroxide and "10 per cent. sodium hydrosulphite powder"; the reduced dye-stuff is diluted to a definite volume, divided into five dye baths, and cooled or heated to the required temperature. The amount of liquor is forty times the weight of yarn in each case. The test revealed three types of dye-stuff, which have been classified as A, B and C. A. Those which dye the 150/36 darker at all temperatures; if the 150/21 and 150/36 are about equal in shade at 60° C., the dye-stuff is classified A60. If the 150/36 is still heavy at 60° C. it is classified A60+. B. Those dye-stuffs which dye the 150/36 darker at 20° C., but at 60° C. dye the 150/21 darker. C. Those which dye the 150/21 darker at 20° C., and become increasingly darker on the 150/21 as the temperature is raised. Examples of classification: A60, Caledon Olive R., A60+, Hydron Yellow NF. B30, Alizanthrene Golden Orange G. B35, Paradone Brilliant Violet R. C, Ciba Brown 2R., and Caledon Jade Green. W. P. S.

New Reaction for Dyestuffs containing Copper in Hair and its Use in the Identification of Dye in Hair. H. Meyer. (*Chem. Ztg.*, 1932, **56**, 95.)—A test tube is half filled with a fresh mixture of 10 parts of 10 per cent. hydrogen peroxide, and 1 part of dilute ammonia, and when effervescence has ceased, a few thin strands of hair, 3 to 4 cm. long, are inserted. In the presence of a dye containing copper (*e.g.* henna), bubbles are evolved, and the liquid becomes warm. Other metals and metal-free colours do not react, and cotton or linen fibres containing a copper colour give much weaker reactions than human hair. The reaction is attributed to catalytic acceleration of the decomposition of hydrogen peroxide by copper, in which it is considered that the keratin in the hair plays a part, probably by reason of the physical nature of the protein molecule; a pronounced reaction is, therefore, characteristic of hair. The method may be used in conjunction with micro-modifications of the ordinary reactions of metals for the diagnosis of hair dyes, and a rapid technique, suitable for a sorting test, is described. It is important that the keratin molecule should be sufficiently decomposed in order to obtain the metal in the free state. This is best achieved by the action of cold fuming nitric acid for 3 minutes, after which the solution may be tested for silver by means of hydrochloric acid, for lead by addition of sulphuric acid, and, after neutralisation of most of the acid, for bismuth by the basic nitrate test. For cobalt the hair should be digested for 5 minutes with warm concentrated acetic acid, and the potassium nitrite test applied. J. G.

Determination of Small Amounts of Acids, Alkalis and Salts in Textiles. A. A. New. (*Text. Manufacturer*, February, 1932.)—Small amounts of acid or alkali may be determined by extracting the textile with water (*p*H should be over 6), taking the *p*H value of the extract, and also titrating the extract to an end-point identical with that of the water used for the test. Plotting of the titration results against the *p*H value frequently gives valuable information. The extract is made with 100 c.c. of water for 5 grms. of material for 1 hour, sometimes at room temperature and sometimes at the boiling-point, any loss by evaporation being made good. For commercial work the simple test-paper method still holds its own. For the determination of salts, it is not enough to determine the ash only. An examination should also be carried out of a boiling-water extract, followed by an extraction with dilute hydrochloric acid, and finally with dilute sodium hydroxide solution. These four preparations are tested qualitatively in the usual manner. R. F. I.

Inorganic Analysis

Qualitative Analysis without Ammonium Sulphide. A. S. Komarowsky and W. J. Goremykin. (*Z. anal. Chem.*, 1932, **87**, 339–342.)—The filtrate from the copper arsenic group, boiled free from hydrogen sulphide, is slowly added to a mixture (proportions not stated) of 20 per cent. caustic soda solution, 10 per cent. sodium carbonate solution, and about 5 c.c. of a 3 per cent. hydrogen peroxide; the mixture is stirred during the addition, boiled, and filtered. The filtrate contains zinc, aluminium, and chromate. The precipitate is extracted by boiling with a mixture of ammonium carbonate and ammonia; nickel and cobalt

dissolve, the latter as a complex ammine, which must be destroyed by evaporation to dryness with strong nitric acid. The insoluble extraction residue is well washed and dissolved in a little nitric acid and hydrogen peroxide. The solution is approximately neutralised with ammonia, made ammoniacal, treated with solid ammonium chloride and with hydrogen peroxide, and heated to boiling; the precipitate contains iron and manganese. The filtrate is treated with ammonium carbonate as usual for the separation of alkaline earths from magnesium. W. R. S.

Benzidine and Tolidine as Reagents in Analysis. R. G. Harry and E. A. Rudge. (*J. Soc. Chem. Ind.*, 1932, **51**, 64–66T.)—*o*-Tolidine may be substituted for benzidine in testing for the presence of per-salts, aldehydes, etc., but it is more affected by the presence of excess of acid. Both substances give blue colour reactions with manganese, iron, chromium, vanadium, and cerium salts. As little as 1 part of ceric ammonium nitrate in 10,000 parts of water gives a distinct coloration with either benzidine or *o*-tolidine, and the reaction may be used for the colorimetric determination of ceric salts in the absence of manganese, iron and chromium. Lanthanum, thorium, zirconium, yttrium and didymium salts do not yield a coloration with the reagents. Benzidine may be used for the determination of formic acid in lead formate. One grm. of the formate is dissolved in 30 c.c. of boiling water, 6 drops of methyl-thymol-blue solution are added, and 0·2 *N* sulphuric acid is added until the indicator turns bright red in colour; 60 per cent. by volume of alcohol is added, the lead sulphate separated by filtration, the filtrate treated with 8 c.c. of 0·92 per cent. benzidine solution (in alcohol), the precipitated benzidine sulphate separated by filtration, and the formic acid in the filtrate is then titrated with 0·1 *N* sodium hydroxide solution. W. P. S.

Electrolytic Determination of Gallium. E. Reichel. (*Z. anal. Chem.*, 1932, **87**, 321–332.)—The sulphate solution (80 c.c.) was treated with 50 c.c. of strong ammonia and 40 grms. of ammonium sulphate, and electrolysed at 60° to 65° C. between platinum gauze cylinders under agitation (1200 R.P.M.) at 5 amp. and 3·5 volts; duration, 20 to 60 minutes for 0·05 to 0·1 grm. of gallium. As neither the ferrocyanide reaction nor other chemical tests appear to be sensitive enough for ascertaining complete deposition, the electrolysate was tested by repetition of the electrolysis after the cathode had been weighed, any fresh increase in weight being noted. When the electrolysis is interrupted, the cathode is quickly immersed in cold water, washed with water, alcohol and ether, and carefully dried. During electrolysis the metal is liquid and silver-white; when washed it becomes solid and bluish-grey. When the deposit is dissolved in strong nitric acid, the platinum cathode shows signs of alloying, as in the case of zinc. The discoloration after acid attack is best removed by strong heating with a Bunsen burner. Appreciable amounts of platinum are dissolved from the anode, and re-deposited on the cathode. These amounts should be ascertained by blank tests, and the necessary correction applied. The anode, as well as the cathode, should be weighed before and after electrolysis. Further tests are in progress.
W. R. S.

Iodimetric Determination of Chromium and Manganese with Persulphate. J. H. van der Meulen. (*Rec. Trav. chim.*, 1932, **51**, 369–373.)—The conversion of bivalent manganese into permanganate by means of persulphate with a silver salt as catalyst, is normally confined, for quantitative purposes, to relatively small amounts of manganese, owing to the liability of manganese dioxide to precipitate when larger amounts of manganese are present; this precipitation with the larger quantities is prevented if either hydrofluoric acid or phosphoric acid, or both, are present. Silver nitrate acts catalytically in accelerating the oxidation by persulphate of tervalent chromium to chromate, and in securing the rapid decomposition of the excess of persulphate. These facts are used in the following process worked out for determining chromium and manganese when present together in a solution: To 25 to 50 c.c. of the solution (containing not more than 0·05 grm. of manganese and 0·075 grm. of chromium, and slightly acid with sulphuric or nitric acid) are added 15 to 20 c.c. of phosphoric acid (25 per cent.), 2·5 to 3 c.c. of "strong" hydrofluoric acid, 10 c.c. of 0·1 *N* silver nitrate solution, and 1·5 grm. of potassium persulphate. The liquid is heated first on a water-bath until evolution of oxygen bubbles takes place, and then gently boiled for five minutes over a gauze. After cooling, 10 c.c. of *N* potassium iodide solution and 5 c.c. of 5 *N* hydrochloric acid are added; after 2 or 3 minutes the liberated iodine is titrated with 0·1 *N* thiosulphate solution (giving manganese and chromium). To a second similar portion of the original solution are added 25 c.c. of water, 2 c.c. of 0·1 *N* silver nitrate solution, 2 grms. of zinc sulphate, 2 grms. of sodium sulphate crystals, and 1·5 grm. of potassium persulphate. The solution is heated on a water-bath until precipitation of manganese dioxide takes place, and then boiled until the excess of persulphate is decomposed; 5 c.c. of *M* manganese sulphate solution are then added, and the boiling continued until the solution shows no trace of pink colour. The precipitate is filtered off on a sintered-glass filter, washed with hot water, and rejected. Ten c.c. of *N* potassium iodide solution and 5 c.c. of 5 *N* hydrochloric acid are added to the filtrate after cooling; it is kept for 2 to 3 minutes, diluted with 50 to 100 c.c. of water, and the liberated iodine is titrated with 0·1 *N* thiosulphate solution (giving chromium alone). One c.c. of 0·1 *N* thiosulphate solution = 1·7334 mgrm. of chromium or 1·0986 mgrm. of manganese. S. G. C.

Determination of Boric Acid in Silicates. E. Schulek and G. Vastagh. (*Z. anal. Chem.*, 1932, **87**, 165–172.)—Reliable results may be obtained by the use of the following method. The very fine powder (0·1 to 0·25 grm.; the authors' aim at 0·01 to 0·035 grm. B_2O_3, with maxima of 0·2 grm. SiO_2 and 0·1 grm. Fe_2O_3) is decomposed by fusion with sodium carbonate. After cooling, 5 to 6 c.c. of water are added, and the melt is completely disintegrated by warming. The crucible contents are quantitatively transferred to a distilling flask, and the crucible is rinsed with a minimum of water (total volume of aqueous liquid, 10 to 12 c.c.). The still is connected with a cooler, the exit tube of which dips into 10 c.c. of *N* sodium hydroxide solution, contained in a 250 c.c. silver dish. A cooled mixture of 200 c.c. of methyl alcohol and 15 c.c. of strong sulphuric acid is admitted through a separating funnel, and the liquid is gently heated until all the alcohol

has distilled over. The silver dish is lowered, and the cooler tube is rinsed with alcohol. A single distillation suffices for glass and enamels. In the case of ferruginous silicates, the operation must be repeated. The flask is cooled, and 100 c.c. of methyl alcohol, together with a little precipitated calcium carbonate (to prevent bumping) are introduced, and the alcohol again distilled off. The distillate is evaporated to dryness, after addition of 10 c.c. of *N* sodium hydroxide and a few drops of 30 per cent. hydrogen peroxide free from phosphoric acid; the residue is fused (with a little potassium hydroxide, if necessary), and the melt is dissolved in a few c.c. of water, faintly acidified with 10 per cent. hydrochloric acid, and, if cloudy, filtered through a small pad of cotton wool into a 50 c.c. conical flask; three washings with water in 2 c.c.-portions are applied. The filtrate (15 to 20 c.c.) is boiled for one minute with coarse pumice powder to expel carbon dioxide, cooled and neutralised with 0·1 *N* alkali against a drop of methyl red indicator. After addition of 2 grms. of pure mannitol and 5 drops of phenolphthalein, the liquid is heated to boiling, and titrated with 0·1 *N* alkali to the first tint of pink. This must persist after addition of 0·5 grm. of mannitol (1 c.c. = 0·003482 grm. B_2O_3). The residual liquid in the still should be tested for complete elimination of the boric acid by another distillation with 30 c.c. of the alcohol and repetition of the above procedure. Complete recovery was effected by single distillation in most cases, and by double distillation in all. A micro-method for 0·0007 to 0·003 grm. B_2O_3 is also described; it follows the lines of the procedure here reproduced. W. R. S.

Microchemical

Vacuum Sublimation under the Microscope. L. Kofler and W. Dernbach. (*Mikrochem.*, 1931, **9**, 345–349.)—A simple apparatus for observing sublimation *in vacuo* under the microscope is made for use with the micro melting-point apparatus of Klein (*Mikrochem. Pregl-Festschrift*, 1929, 192), or with that devised by Kofler and Hilbck (*Mikrochem.*, 1931, **9**, 38). It consists of a square microscope slide, with sides 3½ cm. long. A cover with walls, 6 mm. high, in which is blown a side tube to connect with the vacuum pump, is cemented on to the slide. The top of the cover must be parallel in plane to the slide to avoid distortion of the image. The substance to be sublimed is placed on the slide, and the sublimate is collected on a cover slip, held at a distance of 4 mm. from the slide by means of a small glass or metal ring. The cover slip and metal ring should fit conveniently under the vacuum cover. The whole apparatus is placed on the melting-point apparatus. J. W. B.

Micro-Determination of Carbon by the Wet Method. (Part II). Combustion of Liquids. E. Schadendorff and M. K. Zacherl. (*Mikrochem.*, 1932, **10**, 99–108.)—The micro-method of Lieb and Krainick (*Mikrochem.*, 1931, **9**, 367; ANALYST, 1932, 273) is extended to the combustion of liquids. The method is the same except for the manner of introducing the weighed sample into the combustion chamber. Liquids with a boiling point above 200° C. can be weighed into an ordinary Pregl combustion boat, and placed in the oxidation chamber. Liquids of lower boiling point are weighed into small capillary tubes, 1 mm. in diameter, with a small solid handle at one end, and sealed. The length of capillary

and handle is 4 cm. In order to break the capillary inside the oxidation chamber, the vessel is made slightly pointed, instead of rounded at the bottom, and two small lumps of glass, one above the other, serve to support the capillary in a vertical position when it is dropped, handle downwards, into the vessel. The gas inlet tube is made with a projection at one side, about 1 mm. from the opening, which is about 1·5 cm. from the bottom of the vessel. By rotating the inlet tube the capillary is very simply broken. This is done after the chromate mixture has been added and the baryta introduced into the absorption vessel. Nine different liquids were tested, and excellent results were obtained. The method was also tested on solutions; 0·3 per cent. aqueous solutions of urea gave unsatisfactory results, usually low, but synthetic mixtures of urea, uric acid, hippuric acid, and creatinine in water, in similar proportions to those present in urine, gave good results, with a maximum error of 3 per cent. Determinations were also made on blood serum, and the results agreed with those obtained by the dry combustion (Pregl) method. J. W. B.

Microchemical Determination of Glucose. Ch. Cimerman and P. Wenger. (*Mikrochem.*, 1931, **9**, 295–299.)—The method is suitable for concentrations of glucose of the order of 0·1 to 1 per cent. Fehling's solution is used, the precipitate is centrifuged instead of filtered, and the whole procedure is carried out in one tube. A preliminary determination should be made, and the test solutions appropriately diluted to a concentration of 1 or 0·1 per cent. *Reagents.*—Two copper sulphate ($CuSO_4$, $5H_2O$) solutions, containing, respectively, 34·65 grms. in 500 c.c., and 69·30 grms. in 500 c.c. Two sodium potassium tartrate solutions, containing, respectively, 175 grms. of tartrate and 50 grms. of sodium hydroxide in 500 c.c., and 17·5 grms. of tartrate and 5 grms. of caustic soda in 500 c.c. Approximately 0·5 per cent. solutions of guaiacum in alcohol and potassium cyanide in water. *Method.*—For approximately 1 per cent. solutions of glucose the more concentrated copper sulphate and tartrate solutions are used, and for 0·1 per cent. solutions the more dilute; 2 c.c. of copper sulphate solution, and 2 c.c. of the tartrate solution are placed in the reagent glass of 40 c.c. capacity, with an exterior diameter of 3 cm. The solution is heated to boiling, and the sugar solution is added from a burette until decolorisation is apparent. The tube is then centrifuged for 1 or 2 minutes at a velocity of 2000 to 2500 revolutions per minute. A small drop of the clear liquid is tested for copper by placing it on a filter paper, followed by a drop of the guaiacum solution, and a drop of the potassium cyanide solution. A blue colour indicates copper. When copper is still present, more sugar solution is added, and the solution is again heated to boiling and centrifuged. The method eliminates the possibility of oxidation during filtration, and gives results accurate to a few units per cent. on 0·1 per cent. solution of glucose. Ions that react with potassium cyanide ($Hg^{\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$), or with guaiacum ($Pb^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$), should not be present. Lead may be removed by adding potassium carbonate to the test solution before the determination. J. W. B.

Dry Method for the Micro-Analysis of Gases. F. E. Blacet and P. A. Leighton. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 266–269.)—An apparatus for the micro-analysis of gases is described, together with a method for the analysis

of gas samples of the order of 25 to 100 c.mm. without the use of liquid reagents. Yellow phosphorus is used to remove oxygen, fused potassium hydroxide for carbon dioxide and fused phosphorus pentoxide to remove water vapour. These absorbents are also used in the analysis by combustion of hydrogen, carbon monoxide and methane. The volume of gas is measured in a water-jacketed micro-burette made from a capillary tube about 0·5 mm. in diameter, and accurately ruled in mm. divisions for a length of 45 cm. It is calibrated by weighing drops of mercury; the capacity is approximately 1 c.mm. for 4 linear mm. The lower end of the tube is sealed to a larger tube, containing a trap to keep out any impurities from the capillary during sealing, and this is attached to a short length of heavy rubber tubing, which is filled with mercury and plugged, and clamped in a heavy clamp with a finely-threaded screw, by means of which the level of mercury in the burette may be adjusted. The upper end of the capillary is bent down, and ends in a tip of small outer diameter, which is turned up, and is submerged in mercury in a small reservoir (7 cm. in diameter), which can be raised or lowered. The containers for the gas samples have a capacity of 2 c.c.; they are inverted, and are attached by means of circular steel springs to a revolving table, so that their position can be easily adjusted. For the determination of oxygen in dry air the containers are filled with mercury and then several hundred c.mm. of the gas are added from a glass tube drawn out to a capillary, or by means of a Toepler pump. The burette is next completely filled with mercury, and the tip is brought into the gas sample, and 25 to 100 c.mm. are drawn in by means of the screw, after which further mercury is drawn in, the tube being tapped to prevent sticking, and the volume of gas is read in the calibrated part of the tube. The mean of five independent readings should be taken. The gas is then expelled into a second container, and the oxygen is absorbed by yellow phosphorus, which has been fused into a loop of platinum, and kept under mercury. The platinum wire has a glass holder, by means of which the phosphorus may be placed in position in the holder containing the gas, so that only the phosphorus bead and a little platinum wire enter the gas bubble, without touching the sides of the holder. In most cases the gas is completely absorbed in 15 minutes, but it is safer to draw the residual gas into the burette, take a reading, and again expel it, and allow it to remain in contact with the absorption agent for a further 5 minutes, until the volume is constant. For the absorption of water a bead of fused phosphorus pentoxide, prepared over a glowing electric coil, is used; carbon dioxide is absorbed by fused potassium hydroxide, also prepared over an electric coil, but allowed to collect moisture from the air until the surface is shiny, before it is placed under the mercury in the reservoir. Errors in test determinations were usually less than 1 per cent. J. W. B.

Mill for Small Samples. W. H. Cook, E. P. Griffing and C. L. Alsberg. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 102–106.)—A mill suitable for grinding individual wheat leaves and grains, without loss of substance and moisture, is designed on the general cutting principle of the Wiley laboratory mill (*Ind. Eng. Chem.*, 1925, **17**, 304). A rapid shearing effect is obtained by the action of a hard tooled steel knife with four blades keyed to a shaft, cutting against one

blade of tooled steel placed in the wall of the grinding chamber. The rotating knife also serves to keep the material in motion, and when it has been ground sufficiently, aids in its discharge through a screen in the bottom of the chamber. The main body of the mill consists of a cast-iron block, 2 inches square and 4 inches long, $3\frac{1}{2}$ inches of which are occupied by the bearing for the half-inch shaft. The front half-inch forms the grinding chamber, which is $1\frac{1}{4}$ inches in diameter, and the rotating knife, keyed to the shaft, occupies about three-quarters of its capacity. The length of the rotating blades from the centre of the shaft is $\frac{1}{2}$ inch. A brass tube, $\frac{1}{16}$ inch in diameter, leads into the top of the grinding chamber for introducing the material, and is closed during grinding by means of a solid brass piston. The bottom of the chamber is formed by a copper drawer where the ground material is collected; the top of the drawer consists of a mesh of the desired size. A water-cooling system surrounding the shaft prevents overheating of the material, but may be dispensed with. The capacity of the mill is 5 to 8 kernels of wheat, which are best ground up a little in a mortar before grinding in the mill, and leaves are cut into small pieces. At an operating speed of 5600 rotations per minute, and a clearance of 1/2000 inch between the rotating and stationary blades, a single charge of material is reduced to pass an 80-mesh sieve in from 3 to 4 minutes, and gives a homogeneous sample. (Made by A. H. Thomas & Co., Philadelphia.)

J. W. B.

Micro-Gravimetric Determination of Silica in Tissue. J. C. Morgan and E. J. King. (*J. Biol. Chem.*, 1932, **95**, 613–620.)—The results are given of an attempt to develop a micro-gravimetric method for the determination of silica. The procedure evolved is based on the same chemical principles as the usual gravimetric analysis for silica, but the technique is entirely different. In working out the method, use was made of the apparatus and methods described by Emich [*Lehrbuch der Mikrochemie*, Munich, 2nd edition (1926); *Mikrochemisches Praktikum*, 2nd edition (1931)] and by Pregl (*Quantitative organic microanalysis, translated by E. Fyleman*, London, 2nd edition, 1930, 6, 16); a micro-balance is essential. The precautions necessary and the difficulties encountered are described in detail. The samples of tissue were ashed to remove organic matter by means of ring burners. It was decided to volatilise the silica with hydrofluoric acid, and then determine the silica from the loss in weight on volatilisation. An attempt was made to ash the tissue and treat the ash directly with the hydrofluoric acid, without separating the silica from the other non-combustible substances. However, on addition of acids, the salts formed showed a marked tendency to creep up the sides of the crucible and over the edge, whatever the mode of heating. Therefore, the procedure finally adopted was to ash the tissue, render the silica insoluble, filter off the other substances, and treat the purified silica with hydrofluoric acid. The method of rendering silica insoluble is simply to heat it in acid solution, which at the same time dissolves practically all other material present. The acid commonly employed is hydrochloric, but a more satisfactory agent was found in the dihydrate of perchloric acid, which is a powerful dehydrating agent at its boiling-point, 203° C. By boiling the silica for 15 minutes with perchloric acid, the dehydration is completed, and the mixture does not require to be

evaporated to dryness. After cooling, and the addition of silica-free distilled water, the solution is filtered off. The transference of the precipitate from the crucible was avoided by the method of filtering evolved by Emich, which consists in sucking off the solution through a filter stick. An illustration shows the manner in which this was used. The filter paper left in the crucible was dried, then burned off, leaving the silica in the crucible in a fairly pure state. Its weight was determined by heating until fuming ceased, first with sulphuric acid, and then with hydrofluoric acid *plus* sulphuric acid, the crucible being weighed after each operation. The ring burners used heated the top part of the crucible uniformly by means of flames radiating horizontally inward from a ring surrounding the crucible; they gave a blue flame which could be regulated from the merest glow to a length of one inch. A few typical results are given. The time required to make duplicate determinations on two tissues (four crucibles) was about 8 hours.

P. H. P.

Physical Methods, Apparatus, etc.

Use of Saturated Ammonium Chloride in the Elimination of Contact Potentials. C. N. Murray and S. F. Acree. (*Bureau of Standards, J. Res.*, 1931, **7**, 713–721.)—In *p*H and potentiometric determinations it is usually necessary to allow for or eliminate the small potential difference between electrode liquids of different compositions by (1) calculation (which can, however, only be used in the comparatively few cases where data are available); (2) experimental measurement of the potential; or (3) elimination of the potential by the insertion of a "bridge," composed of a solution of an electrolyte, the ions of which have almost equal mobilities. In case (3) potassium chloride is usually employed, but the authors have tested solutions containing ammonium chloride, since this salt has a higher solubility than potassium chloride, and its ions are almost equal to one another in mobility. Comparisons were made with a new form of double hydrogen electrode-cell, which is described, a dye being added to facilitate observations of the movement of the liquid junctions. It is concluded that solutions of ammonium chloride up to the saturation-point (5·66 *N*) are preferable to potassium chloride, particularly for solutions of low *p*H value, and annul the contact potential to within ± 1·0 millivolt. Mixtures of ammonium or potassium chloride and nitrate in a molar ratio of 1:3 are also satisfactory for solutions of *p*H 3 to 10, since they are stable and the nitrate counterbalances the effect of the slightly higher mobility of the chloride ion. An error of 1 to 2 millivolts, in saturated calomel electrodes, may arise, through the customary use of a layer of potassium chloride crystals over the calomel, and the resulting hysteresis in solubility and potential when the temperature fluctuates; 4 *N* potassium chloride solution (*i.e.* a saturated solution without solid crystals) should, therefore, be employed when the electrode is not used in a thermostat (*cf.* following abstract). J. G.

Estimation of Liquid Contact Potentials with Potassium Chloride and Ammonium Chloride. G. M. Kline, M. R. Meacham and S. F. Acree. (*Bureau of Standards, J. Res.*, 1932, **8**, 101–110.)—The Bjerrum method of correction for contact-potential by extrapolation is liable to errors of 1 to 3 millivolts if used

outside the limits (*e.g.* of concentration) set by Bjerrum. The results have, therefore, been compared with those obtained by the Loomis–Acree method (*cf.* Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532), in which 4·1 *N* (saturated) potassium chloride solution is used, by means of the systems HgCl | 0·1 *N* KCl | *x*KCl | 0·1 *N* HCl–H_2–Pt, and also of systems in which organic acids and acid salts replace the highly ionised hydrochloric acid. The Loomis–Acree method was shown to have greater accuracy, simplicity and rapidity, and being based on experimental results, it avoids the use of uncertain extrapolations. It is, therefore, recommended for general use in order to ensure uniformity of published data, an approximately isoelectric eliminator, such as (3 *N* KCl + *N* KNO_3), being suitable for solutions of *p*H 3 to 10 (*cf.* preceding abstract). J. G.

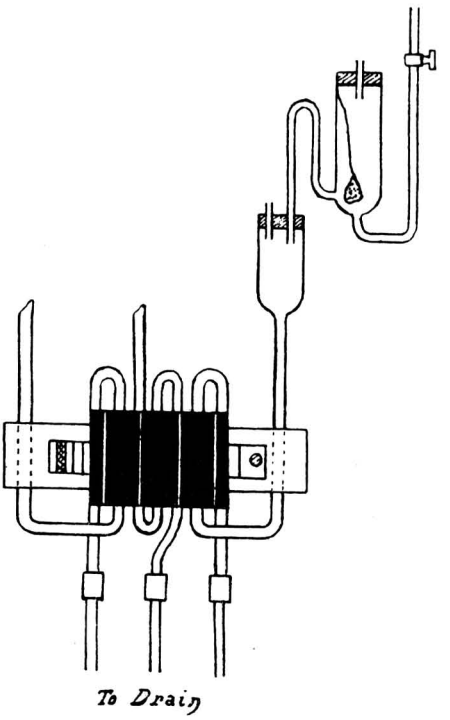
Ventilation of Vehicular Tunnels with Particular Reference to those at Blackwall and Rotherhithe. C. J. Regan. (*London County Council, Annual Report of the Council*, 1930, **4**, Part III. *Public Health—Medical Supplement to the Report on the Hospital Services*, pp. 271–281.)—The exhaust gases from the majority of motor vehicles contain 5 to 9 per cent. of carbon monoxide, but the actual proportion may vary considerably outside these limits, according to the conditions. After consideration of all the pertinent factors, such as the facts that men may be employed on maintenance work for several hours at a stretch, and that long exposure to low concentrations of the monoxide causes far more tissue damage than short exposure to high concentrations, it was deemed advisable that the carbon monoxide content of the air of tunnels, such as those of Blackwall and Rotherhithe, should not be allowed to exceed 20 parts per 100,000.

The following methods were used for analysing the air: (1) The carbon monoxide was determined by Teague's method (ANALYST, 1920, **45**, 459). (2) The suspended matter was determined by means of Owens's portable air-filter, a measured volume of the air being drawn through a small circle of a porous paper disc, and the depth of colour of the circle then compared with a series of shades, one unit of which represents 0·32 mgrm. of black suspended matter per cubic metre of air. It was decided that the average shade of three successive samples taken at short intervals, at any point in the tunnel, should not exceed 6 (1·92 mgrm. of black suspended matter per cubic metre). The actual number of suspended particles was determined with Owens's jet dust counter, a fine ribbon-shaped jet of the moistened air impinging on a microscope cover-glass about 1 mm. in front of the orifice of the jet. The adherent dust particles were then counted under the microscope. (3) Humidity was measured by means of a standard Assmann wet and dry bulb hygrometer. (4) The acidity and sulphur dioxide were determined by passing known volumes of the air through (*a*) hydrogen peroxide solution, and subsequently titrating with alkali, and (*b*) iodine solution, and then titrating with sodium thiosulphate.

In both tunnels, atmospheric conditions are worst at about 10 a.m., and are also worse in summer than in winter, particularly when the temperature of the open air rises above that of the tunnel air, and so decreases natural ventilation. When the average open-air temperature during the 24 hours is above 58° F., the average humidity in the tunnel (for the 24 hours) rises above that of the open air;

otherwise the reverse is normally the case. In no case did the humidity in the tunnel become 100 per cent., so that any foggy conditions which arise are due to smoke fogs, and not to water-vapour fogs. T. H. P.

Automatic *p*H Recorder. C. Morton. (*J. Soc. Chem. Ind.*, 1931, **50**, 436–438T.)—The annexed diagram is an additional illustration to the abstract of this paper. (ANALYST, 1932, 201.) J. G.



Reviews

OFFICIAL AND TENTATIVE METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Compiled by a Committee. Third Edition, 1930 (received December, 1931). Pp. xvii + 593. Published by the A.O.A.C., Washington.

There is no other book quite like this one in the whole range of analytical chemistry. It is essentially a practical treatise—a book for the laboratory bench—and one must not, therefore, expect literary style, nor, indeed, allow one's self to be irritated by the numerous contractions adopted throughout the work. It is a book of methods. It contains no standards, no limits of composition, no typical analyses, and no recommendations other than recommended methods. Its outstanding feature is clarity of composition, and that is of vital importance in

such a compilation. In view of the origin of this book, moreover, no objection can be taken to the occasional use of phonetic spelling.

The aim of the work is to include all the approved methods of the Association for the analysis of agricultural products, and of related substances of importance in agriculture. As is stated in the Preface to the Second Edition, "The methods are the outgrowth of continual critical and collaborative trial . . . participated in by a large number of workers, and undertaken in order to establish the accuracy of analytical results. . . . They are formulated solely by responsible Federal and State officials, acting together, and thus are based on underlying principles of equity. . . ." These methods have consequently been accepted as authoritative in matters at issue before the Federal and State courts in the United States of America. The book sets out to do for American chemists, over a large range of materials, what the Standing Committee on the Uniformity of Analytical Methods of our Society is doing for a limited number of specific products.

A compilation of such authoritative methods, if well done, must have a unique value, and it may be said at once that the work has been ably planned and the scheme most carefully and successfully carried out. The result is a book which no food chemist or agricultural chemist can afford to ignore, and, indeed, the earlier editions of the book are well-known to British workers. It is true that the restriction of the included methods to those of agricultural products—albeit this term is widely interpreted—results in some curious admissions and omissions, but the latter are to be remedied in future editions.

The subject-matter of the book is broadly grouped into two main divisions, the new chapters being denoted here by italics:—NON-FOODS.—Soils; Fertilisers; Agricultural Liming Materials; Insecticides and Fungicides; *Caustic Poisons*; *Naval Stores*; *Paints*; Leathers; Tanning Materials; Plants. FOODS.—Baking Powders; Beverages; Beers, Wines and Distilled Liquors; Coffee and Tea; Cacao Bean and its Products; Cereal Products; Coloring-Matters in Foods; Dairy Products; *Eggs and Egg Products*; Flavouring Extracts; Fruits and Fruit Products; Grain and Stock Feeds; Meat and Meat Products; Metals in Foods; Oils, Fats and Waxes; Preservatives and Artificial Sweeteners; Spices, etc.; Sugar and Sugar Products; and Vegetables and Vegetable Products. There are also chapters on Waters, *Radio-activity*, and Drugs, and 69 pages of tables of reference. The food section of the book (283 pp.) is conveniently arranged in alphabetical order. It is intended in the future to take up similar work in connection with Sewage; Paper; Fibres; Fish; Nuts and Nut Products; Vitamins; and Bacteriological and Microchemical Methods.

The chapter on Soils, though short, is of note, and under the section on the determination of reaction values there are given the pH equivalents in arithmetically-related numbers. Fertilisers are dealt with in 18 pages, and methods for the determination of boric acid are given. The official methods for the determination of potash all involve the use of platinum chloride. There is an excellent chapter of 31 pages on Insecticides and Fungicides, including methods for the determination of arsenic in its various forms in substances such as Paris Green, London Purple, Bordeaux Mixture, and in lead and magnesium arsenates. Methods of analysis of cyanide compounds, of tobacco and extracts of tobacco (in which nicotine is

determined by the silico-tungstic acid method), and of products containing mercury and fluorine, are also included.

In the Foods section of the book, some of the methods familiar to British chemists are given in altered form. The Reichert–Meissl process is carried out by distilling, without first melting the fatty acids, during thirty minutes, and other details of the method differ from the standard process as used here. It may be important to remember this when comparing results obtained in the two countries. The determination of arsenic in meat foods is made by precipitating the magnesium ammonium arsenate and phosphate together; and, after solution of the precipitate in hydrochloric acid, the arsenic is evolved in a modified Gutzeit apparatus, recently-impregnated mercuric bromide papers being used. The presence of aluminium salts in baking-powders is detected by the use of aurin-tricarboxylic acid, which forms a lake with the aluminium salt, and gives a bright red precipitate on addition of ammonia. Artificially-coloured wines, which are notoriously difficult to titrate with an internal indicator, are examined for acidity by making use of a mixture of powdered phenolphthalein and potassium sulphate (1:100) employed as an external indicator.

The book contains a valuable chapter on Colouring-Matters in Foods, including the identification of the dyes and their examination for impurities. The official methods for the determination of added water in milk include the measurement of the refractive index of the serum, on both the fresh and the sour samples, and also the cryoscopic method, of which a very full account is given. A useful qualitative test for mineral acid in vinegar is one employing methyl violet, which gives, with the diluted vinegar, a blue or green colour in the presence of such an adulterant. The methods for the determination of the amount of benzoic acid in foods, depending on solution in chloroform, appear to be simpler and more rapid than some methods in use in this country, and are worthy of trial. Lastly, mention may be made of the micro-chemical tests for the alkaloids, which are described in the section on Drugs. There is a good Index.

Very few errors have been noticed, and most are of a trivial nature; some of them were corrected (as errata) before the book was sent out. The volume, as a whole, has been carefully produced, and the subject-matter is well arranged and copiously cross-referenced. It should be on the bench of every analyst who has to examine the materials dealt with in this compendium of agricultural analytical methods, and, once brought into use, it will rapidly become a much-consulted companion.

ARNOLD R. TANKARD.

SOIL CONDITIONS AND PLANT GROWTH. By Sir E. JOHN RUSSELL, D.Sc., F.R.S. The Rothamsted Monographs on Agricultural Science. Sixth Edition. Pp. vi+636, with Illustrations. London: Longmans, Green & Co. 1932. Price 21s.

One of the most active branches of agricultural science during the present century has been that dealing with soils. Great advances in our knowledge have taken place in a comparatively short space of time, and since the great war soil workers in this country have been greatly influenced by the views of continental, and especially of Russian, workers. A number of international Conferences have

been held, which have brought together soil investigators from all over the world, and many British workers have attended either the sectional Conferences, held from time to time, or the great international congresses, which were held in the United States in 1927, and in Russia in 1931. The result has been a widening of our point of view, and we are no longer in danger of supposing that we can generalise from the soils of the south-east of England to the wide world, or even to the soils of the British Empire, which cover a wider range of climatic and other conditions than those of any single country. This widening of the outlook of British soil scientists is reflected in the new edition of Sir John Russell's great work on Soil Conditions and Plant Growth, which is in many sections a new work. It is not only greatly enlarged compared with the previous edition, but it exhibits clearly the benefits which accrue to workers in soil science from international travel and international congresses. Sir John Russell took part in both the international congresses already mentioned, and he has travelled extensively in the widespread countries of the Empire, and the great experience and knowledge he has gained of the soil conditions of the world are placed at the service of the readers of this work.

The first edition of Soil Conditions and Plant Growth was published twenty years ago as one of the Monographs of Biochemistry, and was a small volume of 168 pages, not much more than one-quarter the size of the present volume. The demand for a work of this kind was shown by the issue of a new impression less than a year later, and by the issue of new editions in 1915 and 1917. All of these issues represented the somewhat narrow British view of soils in which the classical soil of Rothamsted was the centre of the picture, and the soils of the south-east of England filled in practically all the rest. In 1921 and 1927 the fourth and fifth editions were published in the series of Rothamsted Monographs on Agricultural Science, and this new (sixth) edition is in the same series. In these editions the work has been gradually altered and increased, and the present edition is very different in treatment, content and outlook from the early editions.

The general arrangement is somewhat similar to that of the last edition, and the number of chapters is the same, but the Washington and Russian congresses of the International Society of Soil Science have taken place since that volume was issued, and these have had their effect. Large sections have been added which were not in the fifth edition, and many of the old sections have been re-written and re-arranged.

As in all the previous editions, the book opens with a historical chapter, the only chapter that is practically unchanged. The second chapter is on "Soil Conditions affecting Plant Growth," and, though the title is unchanged, the text has been re-arranged and much extended. The third chapter deals with "The Composition of the Soil," and it also has undergone much amendment and extension. Some account of the views of Wiegner and other colloid chemists on the colloid constituents of the soil has been introduced, and all the treatment of soil acidity has been altered and modernised. The section on soil organic matter has been added to, but, though there are further references to the subject in Chapters V and VIII, much recent work on peat and peat soils has not been included. There is a new section on the structure of the soil at the end of this chapter, but this might better have been taken after Russian views on soil profiles and soil types

had been dealt with in the following chapter. This is a very long chapter, and is greatly improved as compared with the previous edition.

The next two chapters have new titles, and IV, now called "The Soil in Nature; Changes in its Mineral Composition," is practically a new chapter. The Russian climatic classification of soils is given, and the Russian nomenclature is adopted to a large extent. Soils are classified into wide belts from a world point of view, according as the climate is hot or cold, humid or arid, and the effects of ground water, topography and vegetation are all considered. Chapter V deals with changes in soil organic matter, and Chapter VI, the title of which is unchanged, deals with the closely related subject of the "micro-organic population of the soil." These chapters are not so much altered, though a considerable amount of new matter, derived from the investigations at Rothamsted and elsewhere, has been introduced. Among interesting new facts, it is stated that four new species of nitrifying organisms, "differing completely from *Nitrosomonas* and *Nitrosococcus*," have recently been discovered at Rothamsted. In this chapter on micro-organisms are included sections on worms and other quite visible invertebrate organisms. The titles of Chapters VII and VIII are unchanged, and a good many of the sections are the same as, or similar to, those in the previous edition, but a considerable amount of new matter is given, such as an account of Dr. Keen's work at Rothamsted on Drawbar pull and its relations to the moisture and calcium carbonate content of the soil. In these chapters the author, in striving after completeness and the inclusion of everything, has included a mixture of analytical matters and questions of nomenclature and soil type, which one would naturally look for in other sections of the book. The concluding Chapter IX is very short, only 7 pages. It is a contrast to all the others in this respect, for they have all been lengthened, while this one has been cut down to less than half. It deals with soil surveys and soil maps, a subject which has been occupying an important place in recent soil meetings and congresses, and on which much more work has been done all over the world than might be supposed from the very slight treatment it receives here.

Soil Analysis, chemical, mechanical and bacteriological, occupies an Appendix of 19 pages. This gives an epitome of the methods usually followed in this country, the methods given being those of the Agricultural Education Association, where such exist.

As in previous editions, a feature of the work is the selected bibliography, in which the authors are arranged alphabetically, and the pages in the text given on which their work is referred to. In addition to this bibliography, which is of great value to the student of soils, very complete references are given throughout the work to the original authorities relied upon for the statements made in the text. The work ends with an index of authors and subjects.

This is a work which contains a mass of information from world-wide sources on the fundamental subject of the soil and its relations to plant life and growth. It is a book which no agricultural teacher or soil investigator can afford to be without. The subject is one in which an immense amount of investigation is being carried out in many countries by chemists, physicists, and biologists, and which is rapidly advancing. No doubt another new edition will be required before

many years are past; the subject is now such a vast and varied one, that the reviewer would venture to suggest that the work should either be divided, or that different specialists should become responsible for the production of different sections. JAMES HENDRICK.

HANDBUCH DER PFLANZENANALYSE. By G. KLEIN, Vienna and Heidelberg. Zweiter Band. Spezielle Analyse. Erster Teil. Anorganische Stoffe. Organische Stoffe I. With 164 illustrations. Pp. 973. Published by Julius Springer, Vienna. 1932. Price unbound, RM.96.

The modern tendency towards specialisation has brought in its train the production of a plethora of books dealing with the chemical methods required in the study of one or other branch of science; such books may be justified on the ground that they save workers in any particular field the time and trouble involved in searching for these methods in separate books, but, on the other hand, the attempt to get all requisite information under one cover, results in the production of rather unwieldy volumes. The book under review is adapted to the needs of those engaged in the analysis of plant materials, and is a compilation in the production of which twenty-three authors have taken part. As may be seen from the title, it forms the second volume of the "Handbuch," and contains only the first part of the section devoted to Special Analysis; as such, it is concerned with inorganic substances, and some only of the organic substances occurring in plants; among the organic substances dealt with are included the alcohols, aldehydes and ketones, phenols and quinones, acids, phosphoric esters of carbohydrate metabolism, lipoids, fats and waxes, phosphatides, phytosterols, sugar alcohols, sugars, and polysaccharides.

Though written by different authors, the sections are similar in general arrangement, and include, in most cases, histological or microchemical methods of investigation. A great many references to original sources are given, and, on the whole, these are well chosen, though individual differences of opinion are bound to occur as to the selection. A special feature is the inclusion in most sections of an account of the occurrence and distribution of the substances dealt with in the various families and genera, written by such an experienced authority as Professor Wehmer. The first part of the book, devoted to inorganic substances, occupies 202 pages, and includes sections on the analysis of the more important kations and anions, on the detection and estimation of ammonia, nitrate and nitrite, on ash analyses in general, and on gas analysis, including both macro- and micro-methods. The book contains a number of illustrations of apparatus and of crystals, etc., and no pains or expense have been spared to make it as nearly complete as possible.

With so much that is excellent, there would seem to be little justification for criticism, but it is difficult to refrain from wondering whether, for example, some of the details of inorganic analysis could not have been left out; so many excellent text-books deal with this subject already. On the other hand, in connection with the descriptions dealing with the occurrence of the sulphate group in plants, we look in vain for any mention of the existence of the carbohydrate esters of sulphuric acid, which have been shown to be important cell wall

constituents of both the red and the brown algae; in this connection it is also worthy of note that another cell wall constituent of the brown algae—mannuronic acid—likewise finds no mention. As a book of reference, this volume is likely to be appreciated by all engaged in the investigation of plant constituents and plant metabolism. P. HAAS.

ERGOT AND ERGOTISM. A Monograph based on the Dohme Lectures delivered in Johns Hopkins University, Baltimore. By GEORGE BARGER, F.R.S. Pp. xvi+279. London and Edinburgh: Gurney & Jackson. 1931. 15s.

There were advantages in living in England, even in the Middle Ages, and one of them was that our people never took kindly to rye, so that this cereal did not become a staple bread-corn, and they escaped the horrors of ergotism. Even Professor Barger's penetrating search into the history of outbreaks of this disease has revealed only one occurrence of typical gangrenous ergotism, near Bury St. Edmunds, in 1762, which was confined to one family, and was possibly due to ergotised wheat, a similar single case in Liverpool, in 1923, due to eating rye-bread, and a mild, but more extensive, outbreak of convulsive ergotism in Manchester in 1927–1929, among a colony of immigrants from Central Europe, who ate bread composed of one part of rye-meal with four parts of wheaten flour. This rye was grown in South Yorkshire, and Professor Barger estimates that the loaves made from it must have contained about 5 grms. of ergot per half-pound loaf.

Owing to this immunity from ergot poisoning, professional interest in this fungus in England has been confined almost entirely to its use as a drug, and, even on this side, has been limited by the fact that ergot and its preparations in the British Pharmacopoeia have not been controlled by any analytical standards. This state of things needs alteration, and if the special Sub-Committee on ergot is successful in getting the recommendations of its recently-issued report adopted, the ergot preparations of the new Pharmacopoeia will at long last be made and controlled in accordance with the new knowledge of ergot, which has accumulated since the discovery of ergotoxine in 1906.

Professor Barger is one of the principal contributors to our knowledge of this drug, and the preparation of this very complete account of ergot and ergotism is not the least of his services in this direction. For analysts the most interesting section will be Chapter VI, dealing with the pharmaceutical and forensic aspects of ergot. This begins with an excellent comparative and critical summary of the treatment of ergot in nineteen different pharmacopoeias, and then proceeds to discuss processes of chemical and biological assay. The quality of ergot is next dealt with, followed by a discussion of the stability of the active principle in the natural drug and in the liquid extract and other preparations, and ending with an article on "ergot and public health," which includes a summary of methods for the detection and estimation of ergot in flour and bread.

Stress is naturally laid in a review in this Journal on the portions of the volume of particular interest to analysts, but it should be added, since analytical work can only be successfully conducted on a basis of sound knowledge, that the book contains a wealth of information on the history of ergot and ergotism, and on the botany, chemistry and pharmacology of the drug. The labour involved in the preparation of the volume must have been enormous, and chemists, pharmacists

and medical men should be grateful to the author for so interesting and complete a presentation of the subject.

The issue of books like this is of no small public service, and it is to be hoped that the enterprise of the publishers will be rewarded by a larger circulation than that provided by the small public to whom the title "Ergot and Ergotism" is likely to make an immediate appeal. T. A. HENRY.

VEGETABLE FATS AND OILS. By GEORGE S. JAMIESON, Ph.D., Chemist in Charge of Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, United States Department of Agriculture. Pp. 444. New York: Chemical Catalog Company, Inc. 1932. Price $6.50.

The editors of the American Chemical Society's series of monographs have been fortunate in inviting Dr. Jamieson to undertake this volume on the chemistry, production and utilisation of vegetable fats and oils, since he is one of the foremost authorities on this subject in the United States. He himself has made notable contributions to recent extensions of our knowledge of natural fats and, still more to the point, he has developed the subject in this book in an exhaustive, modern and accurate manner.

It is not easy to know where to begin with a topic which presents so many angles of approach. Usually one finds, first, an account of the fatty acids, alcohols, etc., which occur in combination in natural fats, then descriptions of how these may be characterised and estimated, and so on, until finally, the ground having been cleared, the description of the fats themselves is reached. Dr. Jamieson, on the contrary, devotes sixteen pages to a rapid, but extraordinarily good, survey of what fats are, where they are found, how and why (in so far as is known) plants and animals produce them, how they are extracted and refined, their nutritive value, and matters such as rancidity and emulsions, and then embarks at once on a description of all the technically important and many of the at present less utilised vegetable fats (255 pp.). The concluding chapters deal with the component fatty acids and alcohols, and also (very fully) with methods of analysis and detection. Naturally, in the brief introduction mentioned, no attempt is made to go into any detail; but different phases (for example, extraction, refining, hydrogenation) are discussed very fully in connection with one or other fat, usually that with which each such phase is most closely connected in American practice, Thus, extraction is dealt with under various oils, refining, especially in the cases of cottonseed, linseed, olive and some others, whilst hydrogenation is included in the cottonseed oil section. Individual taste must largely determine which form of treatment is preferred; the writer can only say that, to him, the method adopted is refreshingly novel, and perhaps more interesting than the more conventional plan. It must be added, however, that a book written on these lines requires ample indexing, with adequate cross-references, and that, in this respect, the existing index should be much extended in order to render rapidly available the very full and up-to-date information scattered throughout the volume.

The vegetable fats themselves are considered under the usual headings of non-drying, semi-drying and drying oils, the individual materials being arranged mainly in alphabetical order of their common names, although here and there

allied groups of fats, such as the chaulmoogra group, the kernel fats of the Palmae, or the Cruciferous seed-fats, are taken together. One wonders whether it is not almost time, in works of this kind, to classify the fats according to their major component acids. If this were done, it would be found, for the most part, that fats with similar applications, would fall together, and also in fairly close alignment with the botanical families from which they originate; whilst it would then be relatively simple, in each group, to consider first the technically important members, and then the less common, but often potentially interesting, ones.

Readers of THE ANALYST will probably be particularly interested in Chapter VI ("Methods"). On the whole, the procedures selected for full description are in accordance with the best standard practice, although possibly more alternatives might have been given, with advantage, in some of the routine methods (such as those for saponification and iodine value, or unsaponifiable matter), in order to cover the entire range of materials which demand consideration. Specific tests (which, of course, abound in this subject) are quoted at length, both in the chapter in question and in earlier parts of the book, under the headings of particular oils; here, again, however, the indexing should be made commensurate with the fullness and accuracy of the matter in the text. Before leaving the critical side of this notice, one must also regret the many lapses of the printer which have been condoned; in most cases they are insignificant and merely annoying, but in some instances might lead to serious misconstruction. Perfect proof-reading of so large a mass of data is admittedly difficult, but without it the value of a book of this kind is apt to be depreciated.

Printer's errors and the adequacy of indexes are, though important, but the mechanical side of book production, and they are given prominence here because this work deserves the best of all the necessary aids to its utilisation. On the other hand, one should acknowledge the very full bibliographical references which are given in the text, not only to original papers in the literature, but also to monographs and articles wherein different aspects of the subject are treated even more fully than in the book itself. The book is written in the light of the most recent work on all the matters dealt with, and is especially helpful because existing information has throughout been considered critically. Dr. Jamieson has not hesitated to point out when, in his opinion, alleged facts require further confirmation before acceptance, and, perhaps most welcome of all, he has ruthlessly eliminated a number of old, familiar statements which have been permitted far too long a residence in the permanent literature of the vegetable fats. The reviewer has rarely had the pleasure of reading such an interestingly presented and exhaustive account of the subject. T. P. HILDITCH.

POTENTIOMETRIC TITRATIONS. A THEORETICAL AND PRACTICAL TREATISE. By I. M. KOLTHOFF and N. H. FURMAN. Second Edition. Pp. 482. London: Chapman & Hall. 1931. Price 36s.

The rapid growth of the subject of potentiometric titrations is exemplified by the fact that, in the second edition of the book at present under review, over thirty-four pages are occupied by references to the literature, whereas, in the previous edition (see ANALYST, **1927**, **52**, 253), only sixteen pages were required.

The book has been extended by 137 pages, although the theoretical introduction has been reduced by 60 pages; thus it is evident that there has been a marked increase, during the past three or four years, in the practical applications of potentiometric titrations. A new and thoroughly up-to-date edition of this excellent book is, therefore, very welcome.

In order to permit the introduction of such a large amount of new material, the authors have been compelled, by the necessity of keeping the volume within reasonable bounds, to omit the first three chapters of the first edition. These chapters dealt with the principles of precipitation, neutralisation and oxidation-reduction reactions, and with electrode potentials and equilibrium constants; in their place has been written a short general introduction to the whole subject of electrometric titrations. This procedure has been justified on the grounds that the same material is adequately discussed in Kolthoff's *Volumetric Analysis*, Vol. I (ANALYST, 1929, **54**, 194), to which the reader is referred. The omission of a large portion of theory means that the book is no longer a complete treatment of electrometric titration, but, in view of the already imposing size of the book and its high price, it is just as well that the theoretical aspects, which can be obtained elsewhere, have been curtailed in favour of the practical information, which is otherwise only to be found distributed throughout a variety of scientific journals. Although a titration is essentially a practical process, it must be admitted that an understanding of the theory of the reaction being used is very desirable, and in this connection the book by Kolthoff and Furman will still prove satisfactory; although the general theory has been curtailed, the theory of each individual titration is given full treatment.

Of the topics dealt with in this new edition, two may be chosen for special mention, since they seem destined to play an important part in the future of the subject; these are the use of the thermionic (wireless) valve and the glass electrode. The treatment in both cases is very good, and references to the literature are given in full.

To those analysts who have already realised the advantages of potentiometric titration it is only necessary to state that the book under review is a very complete account of the subject; to those who have not yet seen the beauty of the electrometric method the book will prove a revelation. S. GLASSTONE.

APPLIED PHARMACOLOGY. By A. J. CLARK, M.C., M.D., F.R.C.P., F.R.S. Pp. x+590. 72 Illustrations. London: Fourth Edition. J. & A. Churchill. 1932. Price 17s.

Professor Clark's book, now a classic of pharmacology, appears in a welcome fourth edition. Two years only have elapsed since the third edition was published, a sign of the rapid progress now being made in "the study of the action of drugs on living tissues."

The chapters on the endocrine glands and on the vitamins themselves bear witness to this progress: they register an advance that is not always credited with its full significance. Hormones and accessory food factors have now ceased to be the monopoly of the physiologist and biochemist respectively; their use by the practising physician brings them into the great category of materia medica. It is

daily becoming more probable that their action in the large doses that the chemist can provide and the pharmacologist assay, is so different in degree from their normal action in healthy metabolism as to be almost a difference in kind. Massive doses of adrenaline or insulin or vitamin *D* may, indeed, produce death, so that precise knowledge of their pharmacology is more than ever necessary.

Professor Clark devotes chapters to subjects as far removed as Disinfectants, Radiation, Immunity, and Respiration. Pharmacology is treated throughout in a way fully justifying the title of his book, with, that is to say, complete practicality. The book is divided into chapters that are, for the most part, based on the organ or organs affected by the drugs discussed—so that we have the pharmacology of the Central Nervous System (four chapters), of the Alimentary Canal (three chapters), of the Circulation (two chapters), and so on. Chapters on the specific therapeutic action of arsenic; mercury, bismuth, and antimony; quinine and emetine: on anthelminthics: and on inorganic metabolism, besides those already mentioned, constitute the bulk of the book, which has also a useful index of fifteen pages and an interesting introductory chapter.

In such a forest of information we may unearth strange and arresting facts by the simple process of browsing. Thus we learn that the rabbit's liver contains an enzyme that destroys atropine, thereby enabling the animal to eat belladonna leaves with impunity; that organic arsenicals must not be given to patients with visceral disease; that iodide prophylaxis may result in hyperthyroidism, so replacing one evil by another nearly as serious; that calcium should be given before using carbon tetrachloride medicinally, as it counteracts the tendency of the latter to produce liver injury; that water poisoning can be produced by the combined action of pituitary extract and water.

Criticisms, so slight as to be negligible, might be made of the statements that "the best methods of drying milk retain about one-half of the vitamin *C* content"; that vitamin *B* "occurs only in the germ of seeds" (what is meant is that in seeds it occurs in the germ only!); that ethyl chaulmoograte is a mixture of the fatty acids of chaulmoogra oil: to the use of C_H values instead of the now universally understood *p*H: to the omission of any discussion of Besredka's so-called "antivirus" phenomena: to the absence of any reference to the action of vitamin *D* on disorders of the peripheral circulation or to the effect of vitamin *B* deficiency on the heart. There are a few minor misprints, such as "acetyl chlorine" for "acetyl chloride" on line 2, page 575.

The lists of preparations given at the ends of chapters, with the approximate costs of the various drugs and galenicals, are particularly original features.

The book should prove highly interesting to many who, perhaps, have no professional use for it. It should prove valuable to all who come occasionally into technical contact with drugs and their effects. It will be indispensable to pharmaceutical chemists, toxicologists, pharmacologists, physiologists, and writers of detective fiction.

A. L. BACHARACH.